Silicon and its impacts on phosphorus in eutrophic freshwater lakes

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Cover picture:
Stephanodiscus parvus diatom frustules in sediment material from Lake Vesijärvi
(Liukkonen et al. 1997).

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Abstract

Some of the less well known aspects of the silicon (Si) cycle in freshwater lake ecosystems were studied in a series of laboratory experiments with surface sediment from four eutrophic lakes in southern Finland. Methodological experiments showed that freezing sediment samples before Si analysis is detrimental, since sub-zero temperatures, particularly combined with large amounts of particulate material, causes substantial complexion of Si, which renders it undetectable by the spectrophotometrical methods normally used for Si analysis. The applicability of the germanium isotope ^{68}Ge as a tracer for Si in experimental sediment research was found reasonable, but methodological problems occurred.

The hypothesis that "the massive sedimentation of diatom blooms in eutrophic lakes may release dissolved phosphorus (P) into the water column through the rapid dissolution of Si and subsequent competitive sorption of the released silicate to anion exchange sites at the sediment surface" was provisionally shown to be correct. Comparatively large additions of inorganic Si were shown to induce desorption of P from hydrated iron and aluminium oxides in surface sediment under laboratory conditions. The experimentally induced mobilisation of P into the sediment interstitial water caused by settled material rich in diatom cells indicated that the proposed pathway of Si input to the sediment surface was possible.

The potential Si-induced release of P was further estimated by combining the experimental results with field data. The magnitude of the studied diatom blooms and the utilisation of Si in the water column showed that release of Si from diatoms at the sediment surface could cause substantial Si pulses within a short period of time. The results also indicated that diatom-derived silicate may induce competitive desorption of P from sediment, and that this phenomenon under certain conditions may be quite a significant source of dissolved P to the water column in the eutrophic lakes studied. The sorption-desorption competitive interactions of Si and P are probably an important factor mainly in the short-term (< one year) cycling of nutrients.

Sammanfattning

Några av de mindre utforskade sidorna av kislets (Si) kretslopp i vattenekosystem studerades i en serie laboratorie-experiment med hjälp av ytsediment från fyra eutrofa sjöar i södra Finland. Metodologiska experiment visade att sediment inte bör frysas innan det analyseras med avseende på lösligt kisel, eftersom temperaturer under noll speciellt i förening med stora mängder partikulärt material förorsakar uppkomst av kiselkomplex som inte går att mäta med vedertagna spektrofotometriska metoder. Ett annat experiment visade att germaniumisotopen ^{68}Ge med vissa förbehåll lämpar sig som marker för kisel i experimentell sedimentforskning.

Experimenten visade också att hypotesen "massiva blomningar av kiselalger i eutrofa sjöar kan frigöra löslig fosfor till vattenpelaren via upplösning av kiselalgernas skal i sedimentets ytskikt och därpåföljande tävlan mellan silikat- och fosfatanjoner" i huvudsak stämmer. Relativt stora tillsatser av inorganiskt kisel visade sig nämligen frigöra fosfor från järn- och aluminiumoxider i ytsediment under laboratorieförhållanden. Eftersom tillsatser av seston som innehöll rikliga mängder av kiselalger också ökade fosforhalten i sedimentets porvatten verkade det som om det hypotetiserade förloppet för tillförsel av kisel till sedimentets ytskikt var möjligt.

Det kisel-inducerade fluxet av fosfor från sedimentet uppskattades vidare genom att kombinera de experimentella resultaten med fältdata. Kiselalgblomningarnas storleksklass samt förbrukningen av kisel i vattenpelaren visade att höga, kortlivade Si-pulser förorsakade av frigörelse av kisel från kiselalger i sedimentets ytskikt är möjliga. Resultaten visade också att kisel från kiselalger kan förorsaka desorption av fosfor från sedimentet, och att detta fenomen under vissa förhållanden kan utgöra en märkbar fosforkälla för vattenpelaren i de studerade eutrofa sjöarna. Samverkningarna mellan kisel och fosfor är sannolikt av betydelse för näringsämnenas kretslopp närmast under kortare (< ett år) tidsperioder.

Tiivistelmä

Piin kiertoa järviekosysteemissä ja erityisesti sen tähän mennessä heikosti tunnettuja puolia tutkittiin laboratoriokokeilla. Tutkimuksessa käytettiin sedimenttiä neljästä rehevästä eteläsuomalaisesta järvestä. Menetelmällisillä kokeilla todettiin, että sedimenttinäytteiden pakastaminen ennen piianalysointia ei ole suositeltavaa. Pakastaminen varsinkin yhdistettynä suureen määrään hiukkasmaista ainesta aiheuttaa piikompleksien syntyä, ja nämä kompleksit eivät ole mitattavissa tavanomaisilla spektrofotometrisilla menetelmillä. Piitä kemiallisesti muistuttava germaniumisotooppi ^{68}Ge todettiin soveltuvan piin merkkiaineeksi myös sedimenttitutkimuksissa, joskin joitain menetelmällisiä ongelmia esiintyi.

Tutkimuksessa testattiin hypoteesiä “laajat piileväkukinnat rehevissä järvissä saattavat hajotessaan sedimentin pintakerroksessa vapauttaa niin suuria määriä silikaattia että liukoista fosforia vapautuu vesipatsaaseen silikaatin syrjäyttäessä fosfaattia pintasedimentin sitoutumispaikoilta ligandinvaihdon kautta” ja todettiin sen pitävän päosin paikkansa. Laboratoriokokeissa suurehkot epäorgaanisen piin lisäykset aiheuttivat fosforin desorptiota pintasedimentin hydratoituneiden rauta- ja alumiinioksidien pinnoilta. Myös piileväpitoisen vajoavan aineksen lisääminen pintasedimenttiin vapautti fosforia huokosveteen.

Piin aiheuttama fosforin vapautuminen järven pohjasedimentistä vesipatsaaseen arvioitiin yhdistämällä laboratoriokokeista saadut tulokset kenttäaineistoihin. Vesistöjen piileväkukintojen laajuuden ja liukoisen piin kulutuksen perusteella arvioitiin, että piin liukeneminen sedimentin pintakerroksesta on ajoittain huomattava. Tulosten perusteella arvioitiin myös, että piilevistä peräisin oleva silikaatti ligandinvaihtokilpailun kautta voi aiheuttaa fosforin desorptiota sedimentistä, ja että tämä rehevissä järvissä tietyissä tilanteissa saattaa olla huomattava vesipatsaan fosforin lähde. Tällaiset vuorovaikutukset ovat todennäköisesti tärkeitä lähinnä lyhytaikaisesssa (alle vuoden kestävässä) ravinteiden kierrossa.

The articles summarised in this thesis

I. Tallberg, P, Hartikainen, H. and Kairesalo, T. 1997. Why is soluble silicon in interstitial and lake water samples immobilised by freezing? Water Research 31:130-134.

II. Tallberg, P., Koski-Vähälä, J. and Hartikainen, H. 2000. ^{68}Germanium as a tracer for silicon fluxes in freshwater sediment. Submitted manuscript.

III. Tuominen, L., Hartikainen, H, Kairesalo, T. and Tallberg, P. 1998. Increased bioavailability of sediment phosphorus due to silicate enrichment. Water Research 32(7):2001-2008.

IV. Koski-Vähälä, J., Hartikainen, H. and Tallberg, P. 2000. Mobilisation of phosphorus from various pools in sediment upon increased pH and silicate concentration. Journal of Environmental Quality (accepted).

V. Tuominen, L., Kairesalo, T., Hartikainen, H. and Tallberg, P. 1996. Nutrient fluxes and microbial activity in sediment enriched with settled seston. Hydrobiologia 335: 19-31.

VI. Tallberg, P. 1999. The magnitude of Si dissolution from diatoms at the sediment surface and its potential impact on P mobilisation. Archiv für Hydrobiologie 144(4): 429-438.

VII. Tallberg, P. and Koski-Vähälä, J. 2000. Silicon-phosphorus interactions at the sediment surface in eutrophic lakes. Submitted manuscript.

Author's contribution

I. The author was responsible for the experimental work and wrote the article. The co-authors contributed to the planning of the study and to the revision of the manuscript.

II. and IV. The author shared the experimental work with J. K-V., was principally responsible for article II, and participated in the writing of article IV. All co-authors planned the study together.

III. and V. The author participated in the planning of the study, in the experimental work, and in the writing of the articles.

VII. The author initiated the study, did the experimental work, and wrote the article together with the co-author.

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1. Introduction

1.1. Silicon chemistry

Silicon (Si) has an atomic mass of 28.09 and is element number 14 in the periodic system, where it is a member of the carbon group (IV) and situated directly below carbon (C, 6), above germanium (Ge, 32), and followed by phosphorus (P, 15). Silicon, like carbon, has a valence of +4, and forms tetrahedral structures with four oxygen atoms; the Si-O (siloxane) bond is one of the strongest chemical bonds in nature (Tan 1994). Silicon occurs in a wide variety of forms: at least in theory in every intermediate form from molecular solubility (i.e. silicic acid or silicate, $Si(OH)_4$) through colloid forms to non-rigid or amorphous and rigid gels (i.e. silicate minerals; Hallmark et al. 1982, Tan 1994).

Silicon is a very common element: it has been estimated that 28 % of the Earth's crust is made up of Si (Jackson 1964), which makes it the second most common element after oxygen (Willén 1991). Most Si is found in silicate minerals, which are chiefly made up of the Si-O tetraeders mentioned above in different configurations and combinations with other elements (Tan 1994). These crystalline minerals, of which the most common is quartz, are characterised by the chemical formula SiO_2 (silica) and are in general very stable. More than 95 % of the rocks on Earth are principally made up of silica (Ingri 1978). Weathering of Si from these minerals takes place mainly over geological time-scales (Lerman 1988). Biogenic silica (opal), which is situated in the amorphous part of the Si spectrum and mainly found in the shells of several different aquatic organisms, has the almost identical chemical formula SiO_2*nH_2O, but is soluble at time-scales ranging from days to years (e.g. Werner 1976, Hurd 1983). In the pH and temperature range (0-30 ºC, pH 6-9; Golterman 1975) and at the concentrations normally found in natural water ecosystems (< 65 mg l^{-1}; Tan 1994) all dissolved Si occurs as silicic acid and its dissociation products, mainly silicate ($SiO(OH)_3^-$). However, at concentrations above 65 mg l^{-1} and under certain other, so far imperfectly understood conditions (possibly complexion reactions with metal ions and organic compounds, Golterman 1975, Tan 1994) polymerisation (or dehydration) of silicate leads to the formation of polymeric colloidal Si ($Si_4O_6(OH)_6^{2-}$, Tan 1994). This colloidal Si is not detectable by common analytical methods for silicate, although it may be available for phytoplankton uptake (Tessenow 1966, Burton et al. 1970, Golterman 1975, Aston 1983).

The geochemical similarities between Si and Ge are well documented (e.g. Goldschmidt 1962, Bernstein 1985, Froelich et al. 1985, Chillrud et al. 1994); the existence of Ge was predicted on the basis of Si properties in the late 19th century, and the new element was provisionally called "ekasilicon". Germanium and Si have the same outer atomic structure, similar ionic radii and occur in solution as similar hydroxides ($Ge(OH)_4$ and $Si(OH)_4$ respectively). Germanium can replace Si in the lattices of minerals and mimic Si in many geological processes (Froelich et al. 1985, Kolodny and Halicz 1988). The similarities between the two elements extend into the biological world, where Ge, concomitantly with Si, is taken up and incorporated into the cell wall by e.g. diatoms (Lewin 1966, Azam 1974, Rivkin 1986). The similarities between the elements has led to the use of ^{68}Ge as an isotope tracer for the much more common element Si in a number of biological studies (Azam et al. 1973, Azam and Chisholm 1976, Rivkin 1986, Ellis and Small 1989, Taylor et al. 1992) since the available Si isotopes until recently have been considered impractical for tracer work (see, however, Brzezinski and Philips 1997). Although Ge is toxic to diatoms in large quantities due to its ability to block the uptake of Si, it is not harmful in trace quantities (Markham and Hagmeier 1982).

The similar properties of Si and P are much more limited despite their proximity in the periodic system, but the existing similarities are large enough to be important in the nutrient budgets of freshwater lakes. While the cycles of the elements are quite different, both are macronutrients capable of limiting the primary production in natural waters, and both produce anions capable of sorption by ligand exchange onto hydrated oxides at e.g. the sediment surface (Brinkman 1993). In boreal eutrophic lakes with sediments rich in iron (Fe), the concentration of Si in the sediment (dissolved and total extractable; Hartikainen et al. 1996) and in the water column (maximal dissolved epilimnetic values; e.g. Willén 1991) are normally about 100 times higher than the respective values for P, however.

Silicon is, further, widely used in Si crystals in e.g. semiconductors and microchips (e.g. Tan 1994, Schulz 1999). Other industrial applications include the silicones, which are products of reactions between silicic acid and various organic molecules, and the numerous uses to which silicate minerals have been put (crystal glass, quartz oscillators, lenses; Tan 1994). Recently, the worlds of biology and physics have started to approach each other, as research into the harnessing of diatom algae for the production of Si structures with applications in the semi-conductor and microchip industries has begun (Morse 1999, Vrieling et al. 1999).

1.2. The Si cycle in water ecosystems

Silicon is required as a macronutrient by certain groups of plants, of which the diatoms *(Bacillariophyceae)*, which account for 25 % of the world's entire net primary production (Willén 1991), are globally most important. Silicon is also a micronutrient for most plants and animals, and recent research has indicated that the importance of Si for terrestrial plants is much higher than previously believed (Epstein 1999). In diatoms, Si is incorporated into the frustule in a complicated protein-sugar template structure (Hecky et al. 1973). Although the high Si requirement is due to this structure and not primarily to metabolic demand the Si requirement is absolute, and a diatom culture deprived of Si will deteriorate even faster than if deprived of P or nitrogen (N; Golterman 1975). The explanations for the existence of the strong Si frustules are largely speculative. Evolutionary pre-determination, i.e. the fact that diatoms evolved from organisms with a functioning Si metabolism already in place, in combination with the fact that the polycondensation of silicic acid into opaline silica is energetically much more favourable than building a shell of calcium or cellulose, seem to be among the most cited (e.g. Raven 1983). Although the absolute Si requirement is an encumbrance under certain conditions, the silica frustule is obviously useful in a number of ways (e.g. defence against grazing, the evolution of sinking as a strategy for more efficient nutrient uptake and survival, increased surface area; cf. Smayda 1970, Margalef 1978, Smetacek 1985, Willén 1991 and references therein).

The average world-wide concentrations of dissolved Si range from 2 mg l^{-1} in the oceans (Treguer et al. 1995) and 4 mg l^{-1} in rivers (Conley 1997) to 6 mg l^{-1} in freshwaters (Aston 1983, Willén 1991). All dissolved Si is however commonly depleted below analytical detection limits (2-10 µg l^{-1}) from the surface waters at times of high diatom production, and the dissolved Si concentration in the alkaline lakes in the African Rift Valley may exceed 100 mg l^{-1} (Gasse et al. 1983, Wood and Talling 1988). The dissolved Si concentrations are usually higher in hypolimnetic than epilimnetic waters due to the regeneration of biogenic Si (and weathering of mineral silicates) from the sediment surface (Aston 1983). In the oceans, the concentrations are highest in estuarine and near-shore areas, where the influence of river discharge and diffuse loading is high, and lowest in the mid-ocean gyres (e.g. Treguer et al. 1995). High concentrations of dissolved Si are also found in sediment interstitial waters (> 40 mg l^{-1}; e.g. Hallmark et al. 1982).

The short-term global Si cycle in the oceans is dominated by the biological uptake of dissolved Si by diatoms and other Si-utilising organisms, and the subsequent regeneration of most of this biogenic Si in the water column and surface sediment (Treguer et al. 1995 and references therein). The inputs of new Si primarily derive from mineral weathering and discharge by hydrothermal vents, and the only significant sink is the semi-permanent burial of some of the biogenically bound Si in the sediments (Treguer et al. 1995). The weathering of most mineral silicates is, however, slow (a magnitude of $6*10^{-14}$ mol cm^2 s^{-1}, Lerman 1988) compared to the dissolution of amorphous, biogenic Si ($2*10^{-9}$ mol cm^2 s^{-1}, Hurd 1983). Since the numbers of Si-utilising organisms (mainly diatoms) are high, the Si cycle is, thus, primarily biological. In freshwaters, the importance of in- and outflow of Si in dissolved or easily regenerable biogenic form (Conley 1997) may be of higher importance (3-20 %; see Willén 1991 for references), but as a rule, the Si cycle is dominated by biological uptake and regeneration within the lake (80 %; Willén 1991). Most of the biological cycle of Si is mediated by diatoms in both oceans and lakes, but radiolarians and silicoflagellates (oceans) and silica-scaled chrysophytes (lakes) may be locally important.

The cycling of Si is, thus, strongly dependent on the role of diatoms in the phytoplankton community structure, on the Si requirements of the dominant species, and on the dissolution of these diatom frustules upon senescence and death. All these factors are, of course, dependent on the physical and chemical as well as on the food web characteristics of the water ecosystem in question. Although diatoms are ubiquitous and contribute to phytoplankton assemblages under very varying conditions, they are more likely to dominate under conditions of low temperature, quite low light, high turbulence and high nutrient concentrations (e.g. Reynolds 1984, Sommer et al. 1986, Willén 1991). In boreal, stratifying dimictic lakes, mass developments of diatoms are thus most likely to occur during spring and/or autumn circulation (Sommer et al. 1986), when the dissolved Si in the water column consequently is depleted to very low levels during a comparatively short period of time, with most of the available Si bound to diatom cells in biogenic form. The overall sedimentation losses of the spring blooms are usually high and the grazing losses small, mainly due to the small overwintering zooplankton populations (Sommer et al. 1986). Aggregation and accentuated sedimentation of the diatom cells in the final phase of the bloom are also common, since diatoms particularly in the senescent phase excrete sticky transparent exopolymeric particles (TEP, Passow et al. 1994), and achieve higher settling velocities than single cells (Kiørboe and Hansen 1993, Passow et al. 1994). Although some of the biogenic Si is regenerated very rapidly in the epilimnion (e.g. Sommer 1984), most of the labile Si in

the ecosystem is thus frequently transported from the epilimnion to the hypolimnion and the sediment surface in a mass event.

The mass sedimentation of diatoms has multiple effects on the cycling of Si and other nutrients and consequently on the development of the seasonal succession of phytoplankton. Since the regeneration of dissolved Si is centred in the hypolimnion during the period of summer stratification, the supply of dissolved Si to the photic layer is limited, which may drastically influence the composition of the phytoplankton assemblage and especially the summer diatom species succession (Sommer et al. 1986, Van Donk and Kilham 1990, Egge and Aksnes 1992). The dissolution of diatom frustules is in addition a very complicated process, which is dependent on among other things pH (Lewin 1961), temperature (Kamatani 1982, Rippey 1983), the species of diatom involved and its physiological state (Lewin 1961), the electrolytic concentration of the surrounding environment (Kamatani 1971, Barker et al. 1994) and the bacterial activity at the frustule surface (Bidle and Azam 1999). Only a comparatively small fraction of the diatoms which reach the ocean sediment floor are permanently buried (< 20 %; e.g. Treguer et al. 1995), and the Si content of these shells as well is usually lowered as the cells are modified by dehydration (Kamatani 1971, Kamatani et al. 1980). It is thus very difficult to make generalisations of the release of Si from diatom frustules. In shallow freshwater lakes, the permanent burial of diatoms may be even smaller (cf. Sommer 1988), and most Si contained in the settling diatom cells is probably released at the sediment surface on a time-scale of days to weeks to months (Hurd 1983, Conley 1997). Since the Si concentrations in sediment interstitial waters as a rule are several times higher than those in the water column (Hallmark et al. 1982), diffusion of silicate from the sediment surface to the hypolimnion is the normal reaction pathway.

While the concentration of silicate in the water column mainly is biologically determined from the input of Si from rivers and the sediment by the difference between uptake and dissolution by diatoms, several other variables and chemical processes (pH, mineralogy, sesquioxide content, organic acids) affect the concentration of silicate in the sediment interstitial water. Especially under areas of high diatom production, equilibrium solubility values for biogenic Si (50-60 mg l^{-1}; Hallmark et al. 1982) may be approached. While some properties of the sediment (e.g. pH) directly influence the dissolution of silica (Hallmark et al. 1982, Tan 1994), the sesquioxide content (oxides, oxyhydroxides and hydroxides of Fe and aluminium (Al); Hallmark et al. 1982) is related to the ability of the sediment to re-adsorb the released silicate (Edwards and Liss 1973, Hallmark et al. 1982, Aston 1983).

Silicate can, like several other anions (e.g. phosphate, sulphate and molybdate), specifically adsorb to the surface of hydrated oxides such as Fe- and Al-oxides by the ligand exchange mechanism, in which hydroxyl groups (OH^-) are exchanged for "foreign" anions (Hingston et al. 1967, Brinkman 1993). Such sorption and desorption mechanisms constitute a buffering mechanism by which the relatively low variation in the dissolved Si content of - particularly - rivers and sediment interstitial waters can be explained (e.g. Edwards and Liss 1973, Aston 1983). A so far little recognised further application of this phenomenon is the competition between different anions, particularly silicate and phosphate, for available sorption sites at the sediment surface (Hingston et al. 1967, Obihara and Russell 1972, Hartikainen et al. 1996).

The capacity of a surfeit of silicate for mobilising phosphate from particle surfaces by competitive desorption has been recognised and utilised for fertilisation purposes in agriculture for several decades (Hingston et al. 1967, Obihara and Russell 1972, Ma and Takahashi 1991). Since P often is the limiting nutrient for phytoplankton production in freshwater lakes, and since large sedimentary reserves and concomitant internal loading of P is a common problem in culturally eutrophicated lakes (e.g. Vollenweider 1975, Sas 1989), any mechanism which accelerates the release of P from the sediment to the water column is of crucial importance for the nutrient budget of the lake. Although the classical theory describing P mobilisation is based on the anaerobic reduction of Fe(III) to Fe(II), whereby soluble Fe and P are released (Mortimer, 1941, 1942), the sorption and desorption of phosphate onto and from hydrated Fe- and Al-oxides may be the main factor regulating the availability of labile P in sediment under aerobic conditions (Hartikainen 1979, Jensen et al. 1995).

The massive sedimentation of diatom blooms in eutrophic lakes with large reserves of P sorbed to the sediment may, thus, through the rapid dissolution of Si and subsequent competitive sorption of the released Si to anion exchange sites at the sediment surface, release dissolved P into the interstitial water and possibly into the water column of the lake. The importance of Si as another important nutrient which may influence the phytoplankton production and species succession makes this connection between the cycles of the two elements even more interesting, especially since it has been shown that eutrophication already affects the relative availability of P and Si in the water column (Officer and Ryther 1980, Conley et al. 1993). Eutrophication actually affects the structure of the phytoplanktonic community through the Si cycle both directly and indirectly (Conley et al. 1993), since cultural eutrophication in general does not involve an increase in the Si loading

(Officer and Ryther 1980). If the Si cycle is in a fairly steady state - i.e. the input of Si is balanced by outflow and by the burial of Si skeletons in the sediment - the increased loading of the other main macronutrients required by phytoplankton, N and P, may directly favour other phytoplankton groups at the expense of diatoms (e.g. Schelske and Stoermer 1971). Increased eutrophication may also increase the production of diatoms to the point where an increase in the semi-permanent burial of diatom shells in the sediment occurs and the Si stock in the water column is depleted (Schelske and Stoermer 1971, Conley et al. 1993), further accelerating the dominance of other, potentially more harmful phytoplankton groups.

1.3. The scope of this study

The first two articles in this thesis are primarily methodological and aim to improve the knowledge of and methods available for biological sediment research concerned with Si. In article I, the effect of sub-zero temperatures on the chemical speciation of Si in sediment is examined. Article II explores the applicability of ^{68}Ge as a tracer for Si in the sediment environment.

In articles II-VII the hypothesis that "the massive sedimentation of diatom blooms in eutrophic lakes may release dissolved P into the water column through the rapid dissolution of Si and subsequent competitive sorption of the released silicate to anion exchange sites at the sediment surface" is examined, and the implications of the phenomenon for the lake ecosystem are discussed. In articles II, III, IV and VII the influence of additions of inorganic Si on the mobility of P in surface sediment under varying environmental conditions is explored in laboratory experiments with and without the aid of isotope tracers. Article III points out the existence of the Si-P interactions in surface sediment, while articles II and IV explore the mechanistics of the Si-induced mobilisation of P from various sediment pools. Article VII examines the relevant concentrations of Si as well as the phenomenon in different lake sediments. In article V (and II), the Si-induced mobilisation of P is further examined through the addition of Si in organic form (as diatoms and as settled seston rich in diatoms) to surface sediment in similar experiments. In articles VI and VII the magnitude of the Si dissolution and P release *in situ* is explored with the aid of experimental results, field data and diffusion calculations. The impacts of the Si-P interactions on the nutrient budgets and the phytoplankton succession of eutrophic lakes are discussed.

2. Study areas

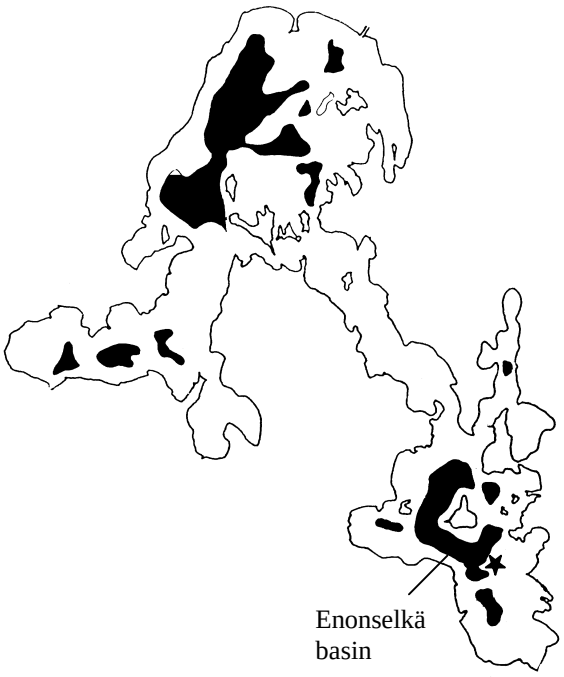
Most of the experimental work in this study was done with surface sediment from Lake Vesijärvi (articles I-VI). In article VII, additional sediment and other data from three other lakes in southern Finland (Lake Hiidenvesi, Lake Tuusulanjärvi and Lake Rusutjärvi) were used. All the lakes are culturally eutrophicated lakes where food web restoration by e.g. intensive fishing has been attempted during the past decades (Horppila et al. 1998, Olin and Ruuhijärvi 1999). The internal loading of P from the sediment remains one of the crucial factors for the succession of the restoration projects.

2.1. Lake Vesijärvi

Lake Vesijärvi (Fig. 1A) is a eutrophicated lake in southern Finland with a surface area of 110 km^2, a mean depth of 6.0 m, a maximum depth of 42 m, and a retention time of 5.4 a. The lake and in particular the Enonselkä basin was severely eutrophicated in the mid-twentieth century (Keto 1982). After reductions in the external loading in 1976 (from 2.1 to 0.2 g P m^{-2} a^{-1}, Keto and Sammalkorpi 1988) the water quality improved, i.e. the total P concentration in winter declined from 150 µg l^{-1} to 50 µg l^{-1} and the Secchi depth increased (Horppila et al. 1998). Cyanobacterial blooms returned in the beginning of the 1980s, however, probably due to internal nutrient loading (Keto and Sammalkorpi 1988, Horppila 1994). A large biomanipulation project in 1989-1993 removed 1000 metric tonnes of fish (mainly roach and smelt; Horppila et al. 1998) and the water quality improved again: the total P concentration has decreased to 30 µg l^{-1} and the Secchi depth doubled to 3.5 m (Horppila et al. 1998). While the biomanipulation project clearly improved the water quality, the exact mechanisms involved remained uncertain, however (Horppila et al. 1998, Kairesalo et al. 1999).

The internal P reserves in the sediment of the lake are still substantial (3 mg P g^{-1} dry sed.; Hartikainen et al. 1996), and the sediment accumulation rate in the deep of the Enonselkä basin has been estimated to be 4-5 cm a^{-1} (Liukkonen et al. 1997) with a gross sedimentation rate of about 60 g dry matter m^{-2} d^{-1} in the area less than 10 m deep (Koski-Vähälä et al. 2000). Two-thirds of the sediment of the Enonselkä basin are at less than 10 m depth (Keto 1973) and not subject to anaerobic conditions during the open-water period if the lake remains in its present state. Although the retention capacity of P by the Lake Vesijärvi sediment is large, due to the high concentration of hydrated Fe-, manganese (Mn)- and Al-oxides (Fig. 1A, Hartikainen et al. 1996), the role of especially aerobic internal loading of P from the sediment remains a crucial questions in the nutrient budget of the lake.

LAKE VESIJÄRVI
(61° 00’ N, 25° 30’ E)



1000 m

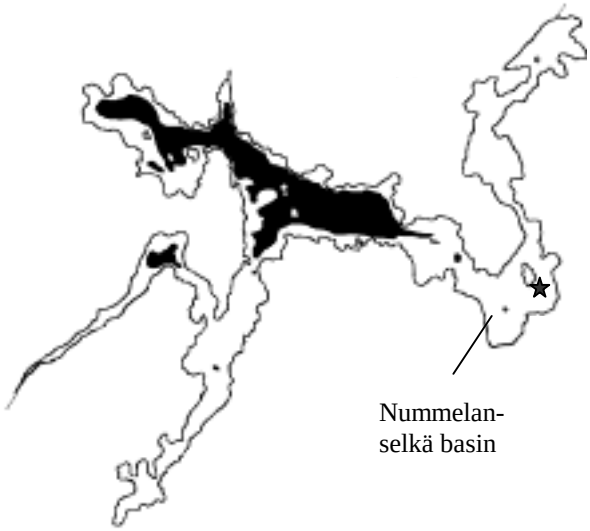
Total area (km^2)	110
Area, Enonselkä (km^2)	26
Retention time (d)	2040
Depth$_{max}$ (m)	42
Depth$_{max}$ Enonselkä (m)	33
Depth$_{mean}$(m)	6.0
Depth$_{mean}$ Enonselkä (m)	6.8
Mean chl **a** (µg l^{-1})	10
Mean total P (µg l^{-1})	30
Tot. P loading (g m^{-2} a^{-1})	0.2
Mean total Si (mg l^{-1})	0.5

Sediment data

Sampling depth (m)	10
Water content (%)	90
Organic matter (%)	12
N (mg g^{-1} dry sed.)	6.5
C (mg g^{-1} dry sed.)	50
Tot. P (mg g^{-1} dry sed.)	3.0
NH_4Cl-P (µg g^{-1} dry sed.)	1.0
NH_4F-P (µg g^{-1} dry sed.)	160
NaOH-P (µg g^{-1} dry sed.)	1100
H_2SO_4-P (µg g^{-1} dry sed.)	460
Fe_{ox} (mmol kg^{-1} dry sed.)	12
Mn_{ox} (mmol kg^{-1} dry sed.)	1.8
Al_{ox} (mmol kg^{-1} dry sed.)	0.7

Data from Keto and Sammalkorpi (1988), Hartikainen et al. (1996), Keto and Tallberg (2000), V, VI.

LAKE HIIDENVESI
(60°22’ N, 24° 12’ E)



1000 m

Total area (km^2)	30
Area, Nummelanselkä	3.6
Retention time (d)	270
D_{max} Hiidenvesi (m)	32
D_{max} Nummelanselkä (m)	6.2
D_{mean} Hiidenvesi (m)	6.6
D_{mean} Nummelanselkä (m)	2.6
Mean chl **a** (µg l^{-1})	27
Mean total P (µg l^{-1})	48
Tot. P loading (g m^{-2} a^{-1})	0.2
Mean total Si (mg l^{-1})	2.5

Sediment data

Sampling depth (m)	4
Water content (%)	82
Organic matter (%)	10
N (mg g^{-1} dry sed.)	3.3
C (mg g^{-1} dry sed.)	27
Tot. P (mg g^{-1} dry sed.)	1.9
Fe_{ox} (mmol kg^{-1} dry sed.)	5.2
Mn_{ox} (mmol kg^{-1} dry sed.)	0.3
Al_{ox} (mmol kg^{-1} dry sed.)	0.8

Data from Olin and Ruuhijärvi (1999), Tallberg et al. (1999),VII.

Figure 1A. Lake Vesijärvi and Lake Hiidenvesi and data concerning their morphology, hydrochemistry and sediments. Areas deeper than 10 m are shaded. The sampling locations are marked by stars (V, VII).

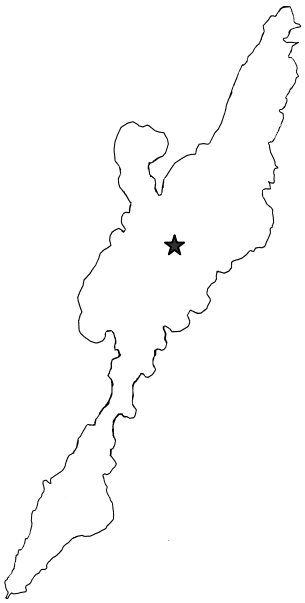
2.2. Lake Hiidenvesi

Lake Hiidenvesi (Fig. 1A) is another eutrophicated southern Finnish lake with a total surface area of 30 km^2, a mean depth of 6.6 m, total P concentrations (epilimnetic maximum values) varying from 50-90 $\mu g\ l^{-1}$ and a total P loading of 0.2 $g\ m^{-2}\ a^{-1}$ (Tallberg et al. 1999). Cyanobacterial blooms have been regular since the 1960s (Harjula 1970, Tallberg et al. 1999). Intensive fishing was started in the lake in 1996, but the results have so far been insignificant. The lake is very turbid (Secchi depth 0.3 - 1.1 m; Tallberg et al. 1999) with a substantially shorter retention time (270 d) than Lake Vesijärvi. Only about 30 % of the lake is deeper than 10 m, and the most eutrophic part of the lake is made up of shallow, nonstratifying areas which to a large extent function as a flow-through system (see Tallberg et al. 1999). High densities of *Chaoborus flavicans* (phantom midge) larvae in the deeper areas of the lake add an unusual dimension to the food web (Horppila et al. 2000). The sediment has a lower total P content (1.9 $mg\ g^{-1}$ dry sed.) and, especially, much less hydrated Fe- and Mn-oxides than Lake Vesijärvi (Fig. 1A). The gross sedimentation rate varied between 21-26 $g\ m^{-2}\ d^{-1}$ dry matter in 1997-1998 (unpublished results). The rate of sediment accumulation was very low in the mid-twentieth century (0.85 $mm\ a^{-1}$, Harjula 1972) and has not increased substantially since then (E. Alajärvi and P. Eloranta, unpublished results).

2.3. Lake Tuusulanjärvi and Lake Rusutjärvi

Lake Tuusulanjärvi (Fig. 1B) is a small (6 km^2), shallow (mean depth 3.2 m, max. depth 10 m) and culturally eutrophicated lake in southern Finland with a total P loading of 0.8 $g\ m^{-2}\ a^{-1}$ (Pekkarinen 1990). The average summer total P concentration is high (94 $\mu g\ l^{-1}$, Pekkarinen 1990, Olin and Ruuhijärvi 1999) and the lake is regularly plagued by cyanobacterial blooms (Pekkarinen 1990). The total P content of the sediment is lower than in Lake Vesijärvi and Lake Hiidenvesi (1.2 $mg\ g^{-1}$ dry sed.), but the contents of hydrated oxides are higher than in Lake Hiidenvesi (Fig. 1). The sediment accumulation rate in the lake was in the range of 1-2 $cm\ a^{-1}$ in the 1980s (Pekkarinen 1990) and the gross sedimentation rate has been estimated to range from 35-55 g dry matter $m^{-2}\ d^{-1}$ during the productive season (Sommarlund et al. 1998).

LAKE TUUSULANJÄRVI
(60°25’ N, 25° 04’ E)



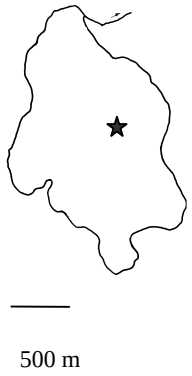
Area (km^2)	6
Retention time (d)	250
Max. depth (m)	10
Mean depth (m)	3.2
Mean chl **a** ($\mu g\ l^{-1}$)	62
Mean total P ($\mu g\ l^{-1}$)	94
Tot. P loading ($g\ m^{-2}\ a^{-1}$)	0.8
Mean total Si ($mg\ l^{-1}$)	1.9

Sediment data

Sampling depth (m)	6
Water content (%)	92
Organic matter (%)	10
N ($mg\ g^{-1}$ dry sed.)	4
C ($mg\ g^{-1}$ dry sed.)	46
Tot. P ($mg\ g^{-1}$ dry sed.)	1.2
NH_4Cl-P ($\mu g\ g^{-1}$ dry sed.)	1.4
NH_4F-P ($\mu g\ g^{-1}$ dry sed.)	110
NaOH-P ($\mu g\ g^{-1}$ dry sed.)	580
H_2SO_4-P ($\mu g\ g^{-1}$ dry sed.)	390
Fe_{ox} ($mmol\ kg^{-1}$ dry sed.)	9.0
Mn_{ox} ($mmol\ kg^{-1}$ dry sed.)	0.6
Al_{ox} ($mmol\ kg^{-1}$ dry sed.)	1.0

Data from Pekkarinen (1990), Tolonen et al. (1990), Olin and Ruuhijärvi (1999), VII.

LAKE RUSUTJÄRVI
(60°26’ N, 24°59’ E)



Area (km^2)	1.4
Retention time (d)	350
Max. depth (m)	3.5
Mean depth (m)	2
Mean chl **a** ($\mu g\ l^{-1}$)	46
Mean total P ($\mu g\ l^{-1}$)	45
Tot. P loading ($g\ m^{-2}\ a^{-1}$)	0.2

Sediment data

Sampling depth (m)	3
Water content (%)	95
Organic matter (%)	23
N ($mg\ g^{-1}$ dry sed.)	21
C ($mg\ g^{-1}$ dry sed.)	110
Tot. P ($mg\ g^{-1}$ dry sed.)	0.9
NH_4Cl-P ($\mu g\ g^{-1}$ dry sed.)	0.8
NH_4F-P ($\mu g\ g^{-1}$ dry sed.)	54
NaOH-P ($\mu g\ g^{-1}$ dry sed.)	350
H_2SO_4-P ($\mu g\ g^{-1}$ dry sed.)	250
Fe_{ox} ($mmol\ kg^{-1}$ dry sed.)	11
Mn_{ox} ($mmol\ kg^{-1}$ dry sed.)	0.3
Al_{ox} ($mmol\ kg^{-1}$ dry sed.)	1.0

Data from Tolonen et al. (1994), Olin and Ruuhijärvi (1999), VII.

Figure 1B. Lake Tuusulanjärvi, Lake Rusutjärvi and selected information about their morphology, hydrochemistry and sediments. The sediment was sampled from the locations marked by stars (VII).

Lake Rusutjärvi is a very small, shallow lake (area 1.4 km^2, mean depth 2 m, Tolonen et al. 1994) which drains into Lake Tuusulanjärvi and is slightly less eutrophicated (total P loading 0.2 g m^{-2} a^{-1}; Tolonen et al. 1994). The mean total P concentration in summer is around 60 µg l^{-1} (Tolonen et al. 1994, Olin and Ruuhijärvi 1999). The total P content of the sediment is lower than in the other lakes (0.9 mg g^{-1} dry sed.) although the concentration of hydrated oxides is high (Fig. 1B, Tolonen et al. 1994). The sediment accumulation rate in the lake was slightly less than 1 cm a^{-1} in the 1980s (Tolonen et al. 1994).

3. Materials and methods

3.1. Sediment sampling

All the sediment used was sampled with a slicing Limnos corer (Limnos Ltd, Finland) from the uppermost 0-1 or 0-2 cm sediment layer. The sediment sampling locations (Fig. 1) were chosen to represent areas where no summertime oxygen depletion of the hypolimnetic water and the sediment surface normally occurs, and where the sediment surface consequently can be regarded as aerobic. Several samples were bulked and homogenised by careful mixing, and the sediment was stored in 0.5 l polyethylene containers in the dark at +2-+4 ºC. The Lake Vesijärvi sediment was taken from 10 m depth in the Enonselkä basin at several different times from May 1994 to May 1997. In Lake Hiidenvesi (Nummelanselkä) the sampling depth was 4 m (July 1999), in Lake Tuusulanjärvi 6 m (June 1996) and in Lake Rusutjärvi 3 m (July 1999).

3.2. Si analyses

Two analytical methods were used to determine the concentration of dissolved Si. Atomic adsorption spectrophotometry (AAS) at a wavelength of 251.6 nm was used to determine the concentration of Si in the interstitial water and other sediment extracts in articles I - V. The dissolved Si in lake water (articles I, VI-VII) and interstitial water (article VII) was measured spectrophotometrically at 815 nm using the blue ammoniummolybdate reaction according to Mullin and Riley (1966) as described by University of Lund (1988). Although the quantitative determinations of e.g. biogenic and total Si are problematic and often depend on the extractants used (e.g. Hallmark et al. 1982, Conley 1998), the analysis of dissolved Si is relatively straightforward (but see I), and the results obtained by AAS and spectrophotometer compared reasonably well. The relative merits of the methods and possible sources of error

are described in detail by e.g. Babko and Pilipenko (1974) and Hallmark et al. (1982). Although both P and Si may interfere in the spectrophotometric analysis of the other element (e.g. Hallmark et al. 1982), the concentrations of P encountered in this study were too low relative to the concentration of Si for P to interfer with the analysis of Si. The interference of Si in the P analysis was corrected for (IV).

All concentrations of Si are given as µg, mg or g Si. 1 g l^{-1} Si = 2.143 g l^{-1} SiO_2 = 0.0357 mol l^{-1} $Si(OH)_4$ (M); see Willén (1991). **Si** denotes the element silicon and is also generally used, **silicate** equals (ortho- or mono-) silicic acid ($Si(OH)_4$ or $H_3SiO_4^-$) or the silicate anion ($SiO(OH)_3^-$), and **silica** means silicon dioxide or SiO_2. **Silicates** are mineral forms of silica (e.g. quartz). Biogenic or opaline silica, sometimes also referred to as amorphous silica, represents the form of silica (SiO_2*nH_2O) biologically incorporated into e.g. diatom cell walls.

3.3. Freezing-induced differences in measurable Si concentrations

The immobilising effect of low temperatures on the measurable amount of dissolved Si in sediment interstitial water was investigated by freezing (-18°C) a series of sequentially filtered interstitial water (May 1995 and November 1994 sediment) and lake water samples from Lake Vesijärvi for periods ranging from 24 h to 8 d. Standard solution of Si ($SiCl_4$) was added to some of the samples prior to freezing, and the impact of very low (< 2) pH values on the process was also studied using separate samples. The samples were either not filtered (1) or filtered through 0.2 µm polycarbonate filters (2), through 100 000 dalton ultrafiltration membranes (3), or through 10 000 dalton ultrafiltration membranes (4). The samples were analysed for Si (by AAS) both before and after freezing. After thawing, the unfiltered samples were filtered through 0.2 µm polycarbonate filters and analysed once more for Si.

3.4. The applicability of ^{68}Ge as a tracer for Si in sediment

The applicability of ^{68}Ge as a tracer for Si additions in sediment was studied by exploring the distribution of additions of either deionized water (control) or of unlabelled and ^{68}Ge-labelled inorganic Si (a solution of 940 mg l^{-1} Si), or diatoms ($3.2 \cdot 10^6$ cells l^{-1}) in surface sediment (Lake Vesijärvi, May 1997). The solution used in the inorganic Si treatment was made by adding the ^{68}Ge-label (20 µl; $^{68}GeCl_4$ 1 µCi ml^{-1}, in 0.5 M HCl, Wallac) to a solution containing 940 mg l^{-1} Si ($NaSiO_3 \cdot 9H_2O$ dissolved in deionized water) whereafter the solution

was left to equilibrate for 4 h. The diatom cultures were labelled by adding the ^{68}Ge-label (32 µl) to 11 ml of distilled water. After 4 h, this solution was added to 1700 ml of *Stephanodiscus hantzschii* Grunow culture (CCAP collection, strain no. 1079/4, grown in the CCAP diatom medium; Beakes et al. 1988), 8 h before the sediment labelling. The surplus ^{68}Ge was removed from the solution by washing with deionized water (10 ml) and centrifuging the cells twice.

The experiment was carried out by adding either (1) deionized water (control), (2) unlabelled or ^{68}Ge-labelled inorganic Si solution (inorganic Si), or (3) unlabelled or ^{68}Ge-labelled diatoms (diatom) to surface sediment samples. The volume of sediment was 15 ml (unlabelled samples) or 10 ml (labelled samples) and the volume of the addition was 0.75 ml (unlabelled samples) or 0.5 ml (labelled samples). The samples were incubated in 20 ml polyethylene scintillation bottles, covered with punctured Parafilm membranes and stirred at 170 rpm for 24 h at 10°C. After 24 h the sediment interstitial water was collected by centrifugation (2350g) and filtration (0.2 µm cellulose nitrate filters). The ^{68}Ge labels and the Si in four sediment fractions were extracted sequentially from 1 ml of sediment using the method introduced by Chang and Jackson (1957) as modified by Hartikainen (1979). The procedure characterises the sedimentary P (or Si; Hartikainen et al. 1996) which potentially takes part in ligand exchange reactions; for further details see Hartikainen (1979) and Hartikainen et al. (1996). First, the soluble P and Si and the exchangeable Ca were removed by extraction with 1M NH_4Cl. Thereafter the fraction presumed to be bound by Al was extracted with 0.5 M NH_4F, the fraction bound by Fe with 0.1 M NaOH and the Ca-bound fraction by 0.25 M H_2SO_4. The ^{68}Ge activities in the extracts were determined by liquid scintillation counting (Wallac, Rackbeta) and the Si concentration by AAS.

3.5. The influence of inorganic Si additions on the distribution of P between different sediment pools

3.5.1. A P and P+Si dual labelling study

The impact of an inorganic Si addition on the distribution of P in surface sediment from Lake Vesijärvi was studied by labelling sediment subsamples (May 1995) with ^{33}P (III). The samples were left to equilibrate for 4 d, whereafter they were enriched with ^{32}P or ^{32}P+Si and the distribution of the isotopes were followed for the next 15 d. First, the ^{33}P (in dilute HCl, carrier free, 370 MBq ml^{-1}, Amersham) was added to the sediment (15 ml of sediment in 20-ml plastic bottles) at a concentration of $1.38*10^6$ dpm per bottle. Pieces (1.5*3.0 cm) of anion

exchange resin-impregnated membrane (type 204-U-386, Ionics, Watertown, MA), which had been pre-saturated in 1 M NaCl for a few days, were then added to half of the bottles. After a four-day equilibration period, the first set of replicates was analysed to determine the distribution of the ^{33}P (day 1). The next day, the samples were enriched with a 1 ml solution containing either ^{32}P-labelled P (an enrichment of 60 µg P as K_2HPO_4 per l sed.) or ^{32}P-labelled P + Si (60 µg P as K_2HPO_4 + 9 mg Si as Na_2SiO_3 per l sed.). The ^{32}P (in dilute HCl, carrier free, 370 MBq ml^{-1}, Amersham) was added at a concentration of 1.56 $*10^6$ dpm per bottle. The sediment sample bottles were covered with punctured Parafilm membranes, and the incubation was performed in the dark at room temperature (24 ºC) under continuous stirring (170 rpm).

Samples were taken on days 1, 2 (2 to 4 h after the additions), 3, 8, 11 and 15. Firstly, 2 ml of sediment was removed from the labelled bottles and the ^{33}P and ^{32}P in particulate material was extracted with 0.1 M NaOH (Schnitzer 1982). The interstitial water was extracted by centrifugation and filtration (0.2 µm, cellulose nitrate filters). The pieces of resin were removed from the resin-containing bottles, rinsed with deionized H_2O, and extracted with 1 M NaCl for 1 h. The inorganic P in these three P fractions (NaOH-extractable P, resin-P and soluble P) was separated from the organic P by selective precipitation of orthophosphate with tungstate, tetraethylamine and procaine under acidic conditions (Bochner and Ames 1982) as described by Orrett and Karl (1987) and Istvánovics (1993). The inorganic P was calculated as the difference in activity between the samples before and after the Bochner-Ames precipitation. The ^{33}P and ^{32}P activities were measured from the extracts using a liquid scintillation counter (Wallac 1411) and HiSafe3 (Wallac) scintillation cocktail. It should be noted that the NaOH-fraction in this experiment (III) and in the experiment with phytoplankton cultures (V) is comparable to the sum of the NH_4Cl-, NH_4F- and NaOH-fractions used in articles II and IV, and not to the NaOH-fraction only (see Hartikainen 1979 and Schnitzer 1982).

3.5.2. A Si, pH and Si+pH fractionation study

The impact of two different-sized Si additions on the distribution of P between five sediment fractions at normal (7) and raised (9) pH was studied in a similar experiment (IV). Firstly, half of a batch of 15 ml sediment samples (Lake Vesijärvi, May 1997) received an addition of 40 µl 4 M NaOH which raised their pH from around 7 to about 9. Then, all the samples were enriched with 0.75 ml of either deionized water (control) or with solutions of 6.9 mg l^{-1} Si as

Na_2SiO_3 (small Si addition) or 940 mg l^{-1} Si (large Si addition). All samples were incubated for 24 h at 10 ºC in plastic scintillation bottles under continuous stirring.

Four inorganic P fractions (Chang and Jackson 1957, Hartikainen 1979) were extracted from the samples one day after the Si enrichment as described in section 3.4.; the interstitial water was collected from another subsample by centrifugation (2350 *g*) and filtration (0.2 µm, cellulose nitrate filter). The fractionation extracts were analysed for P with an ammonium molybdate-stannochloride method (Kaila 1955) and the interstitial water with a molybdenum blue-ascorbic acid method (Murphy and Riley 1962) with an auto-analyser (Lachat quick 8000). The results were corrected for the interference by Si. The Si concentration of the extracts was determined by AAS. Hydrated oxides of Fe, Al and Mn were extracted from separate sediment samples for 2 h with 0.05 M NH_4-oxalate (pH 3.3) at a sediment to solution ratio of 1:20.

3.5.3. Different Si additions and lake sediments

Inorganic Si additions ranging from 0-50 mg l^{-1} sed. were added to surface sediment samples (1) to explore the sorption-desorption processes involved and (2) to check whether different-sized Si-additions mobilised P in surface sediment from other eutrophicated lakes than Lake Vesijärvi (VII). All experiments were conducted in plastic bottles to which 15 ml sediment and 0.75 ml Si solutions of various strengths were added. The bottles were covered with punctured Parafilm membranes and incubated at room temperature during continuous mixing (308 rpm). The Si solutions (0-1000 mg l^{-1}) were produced by adding Na_2SiO_3 to deionized water. The sediment interstitial water was extracted by centrifugation (2350 *g*) and filtration (0.2 µm, cellulose nitrate filter). The filtrate was thereafter analysed for dissolved P (molybdenum blue-ascorbic acid method; Murphy and Riley 1962) and Si (spectrophotometric method). The incubation period was 24 h except in sub-experiment 1, and the interference of Si in the P analysis was corrected for (IV). Although P may interfer in the spectrophotometric analysis of Si, as well (e.g. Hallmark et al. 1982), the concentrations of P were too low for this phenomenon to be of importance.

In the first sub-experiment, the sorption-desorption process was explored by incubating Lake Vesijärvi sediment (May 1995) to which either 0 or 40 mg l^{-1} sed. of Si had been added for 0, 1, 18, 27 and 48 h, respectively. In the second sub-experiment, solutions containing 0 (= deionized water), 200, 400, 600, 800 and 1000 mg l^{-1} Si, producing concentrations of 0-50 mg

l^{-1} sed., were added to sediment from all four lakes in order to find out at which concentration range and in which sediments P was mobilised. Additional Si concentrations (also 1.25, 2.5, 5 and 7.5 mg l^{-1} sed.) were added to the Lake Vesijärvi sediment samples (May 1995). The P mobilised into the interstitial water was plotted against the Si added to the sediment and a function for the P mobilisation was obtained using linear least squares regression. In addition, the concentrations of hydrated oxides of Fe, Al and Mn were determined from the sediments of Lake Hiidenvesi and Lake Tuusulanjärvi as described above (section 3.5.2.).

3.6. The influence of diatom additions on the mobility of P in surface sediment

3.6.1. Cultured phytoplankton

The influence of an addition of biogenic Si in diatom form on the mobility of P in surface sediment was tested in a two-part experiment (V). In the first part, 1 ml of ^{32}P-labelled cultured diatoms (*Stephanodiscus* spp. and *Nitzschia* spp. cultivated from the surface sediment of Lake Vesijärvi) or cyanobacteria (*Microcystis* sp., a pure laboratory grown strain obtained from the HAMBI collection at the University of Helsinki) were added to 15 ml of Lake Vesijärvi surface sediment (May 1995) pre-labelled with ^{33}P (see section 3.5.1.). The chlorophyll *a* concentrations (extracted with ethanol, spectrophotometric determination) of the phytoplankton cultures were 119 µg chl *a* l^{-1} (diatoms) and 670 µg chl *a* l^{-1} (cyanobacteria). The cultures were labelled by the addition of a trace concentration of ^{32}P and left to equilibrate for 24 h. After the addition of the labelled cultures, the experiment proceeded as reported in section 3.5.1. The bacterial activity in the samples was measured as L-[U-^{14}C]leucine uptake (11.7 GBq $mmol^{-1}$, Amersham, Tuominen 1995). The [^{14}C]leucine was added at the saturation level concentration (13.7 µM; Tuominen 1995) and the incubation lasted for 15 min at 20 ºC.

3.6.2. Settled seston

In the second part of the experiment, settled seston which had been collected from the same area of Lake Vesijärvi as the sediment samples was added to surface sediment samples (May 1994) and the effect on the P concentration in the interstitial water was studied. The material was collected in 1994 using sediment traps (polycarbonate tubes; diameter 5.5 cm, height 41 cm) placed at a depth of 9 m, about 1 m above the lake bottom. Seston from three periods was used: 4-31 May 1994 (material from two consecutive 2-week periods mixed; 'May-material');

28 June-12 July 1994 ('July-material'); and 9-24 August 1994 ('August-material'). The amount of diatoms was microscopically enumerated from the settled seston, and was clearly highest in the May-material, both as cell numbers and as Si content (conversion factors from Golterman 1975), and lowest in the July-material (Fig. 9). In May, small (Ø < 10 µm) centric diatoms (*Stephanodiscus* spp.) were the dominant species, whereas the proportion of larger, pennate species increased towards the end of the summer (e.g. *Diatoma* and *Fragilaria* spp.; cf. Liukkonen et al. 1993).

The incubation was performed in large polypropylene syringes, which were filled with 90 ml of sediment and 5 ml of settled material; control syringes were filled with 95 ml of sediment. 10 ml of air was left in the syringes as an O_2 reserve, and through daily changing of this reserve the syringes were prevented from going anaerobic. The syringes were placed in a horizontal position on a magnetic stirrer, and the 5-day incubation was performed in the dark at room temperature (21-23 ºC) with gentle stirring at 1 min on/off intervals (magnetic stirring bars). In the beginning and at the end of the experiment the interstitial water was extracted from the sediment by centrifugation (5 min, 1500 *g*) and filtration (0.2 µm polycarbonate filters). The filtrates were stored frozen until the analyses of dissolved P (molybdenum blue-ascorbic acid method; Murphy and Riley 1962) using an AKEA automatic analysing system (Instrumentarium/Datex). The bacterial activity was measured as described above (section 3.6.1.)

3.7. The magnitude of Si dissolution from diatoms at the sediment surface

The magnitude of diatom dissolution at the sediment surface was assessed with the aid of field diatom and Si data in Lake Vesijärvi (VI) and in Lake Vesijärvi, Lake Hiidenvesi and Lake Tuusulanjärvi (VII). Data on the phytoplankton composition was collected from Lake Vesijärvi in 1982-1995, from Lake Tuusulanjärvi in 1997 and from Lake Hiidenvesi in 1997-1999. The concentration of diatom frustules was microscopically enumerated (Utermöhl 1958) from the surface water samples and from surface sediment samples (Lake Vesijärvi only) taken at the same times. The phytoplankton data from Lake Tuusulanjärvi was provided by the Finnish Environmental Institute, and the data from Lake Vesijärvi (1982-1994) by the City of Lahti (see also Keto and Tallberg 2000). The dissolved Si concentration in the water column was determined in Lake Vesijärvi in 1995, in Lake Hiidenvesi in 1998-1999 and in Lake Tuusulanjärvi in 1997.

The potential daily pulse of Si (equations 1-4) caused by dissolution of diatom frustules at the sediment surface in Lake Vesijärvi (VI) was calculated based on three measured variables: (A) The utilisation of dissolved Si in the water column, (B) the standing stock of diatoms in the water column during the spring bloom, and (C) the diminishing number of diatom frustules enumerated from the surface sediment in May-June. For Lake Hiidenvesi and Lake Tuusulanjärvi (VII), only methods (A) and (B) were used.

Daily Si pulse (mg m^{-3} sed. = µg l^{-1} sed.) = $\frac{Si * R}{D_s}$ (1)

$Si_{water\ deficit}$ (mg m^{-2} sed.) = $C_s * D_p$ (2)

$Si_{diatom\ bloom}$ (mg m^{-2} sed.) = $D_p * \left(\sum_{i=1}^{n} Cd_i S_i \right)$ (3)

$Si_{sediment}$ (mg m^{-2} sed.) = $\left(\sum_{i=1}^{n} Cds_i S_i \right)$ (4)

Si = $Si_{diatom\ bloom}$, $Si_{water\ deficit}$, or $Si_{sediment}$
R = dissolution rate of diatom cells (% d^{-1})
D_s = sediment surface layer depth (m)
C_s = deficit of silicate in the water column (mg m^{-3})
D_p = depth of productive layer (m)
Cd_i = concentration of diatom cells in the productive layer for species i (cells m^{-3})
S_i = Si concentration of individual diatom cell of species i (mg $cell^{-1}$)
Cds_i = the number of diatom cells of species i in the sediment surface layer

In method (A) the pulse estimate was calculated by assuming that all the Si that disappeared from the water column in spring (C_s, equation 2) was taken up by diatoms and that all these diatoms settled out of the water column and dissolved in the sediment surface layer. In method (B) it was assumed that all the diatoms in the water column at the height of the spring bloom (C_d, equation 3) settled out of the water column and dissolved likewise. In method (C) the diatom-bound Si in the sediment surface layer (Cds_i, equation 4) was calculated from the maximal numbers of diatom cells. The dissolution rate R was assumed to be either 3 % d^{-1} for the larger, more heavily silicified cells (VII) or 5 % d^{-1} for smaller, e.g. *Stephanodiscus* spp. cells (VI, VII); in article VI, a total Si pulse (R= 100 %) was also calculated. These dissolution rates were chosen based on the disappearance rate of the small centric diatom cells from Lake Vesijärvi sediment (VI) and the data on dissolution of mixed diatom assemblages compiled by Sommer (1988). The surface sediment layer depth (D_s) was assumed to be 1-10 cm (VI) or 1 cm (VII).

The average Si content of the average diatom cell was calculated using the formulas:

$\log_{10}$Si (pmol Si) = (1.03±0.06)$\log_{10}$V-(2.45±0.19) (Conley et al. 1989, VI, VII) and (5)

$\log_{10}$Si (pg Si) =0.707 $\log_{10}$V-0.263 (Reynolds 1986, VI), (6)

where V= cell volume.

The depths of the productive layers in the lakes (D_p) were estimated as 1.7*Secchi depth according to Reynolds (1984). The mixed layer depth was estimated based on the temperature profile and differed for Lake Vesijärvi in articles VI and VII.

3.8. The potential impact on the mobilisation of P

In article VII, the potential Si dissolution scenarios (section 3.7.) were combined with the obtained regressions between added Si concentration and mobilised P in the interstitial water (section 3.5.3., VII) and used to estimate the possible release of P into the water column using Fick's first law of diffusion (Berner 1976) as described by Gonsiorczyk et al. (1997):

$$J = \phi D_x \frac{dc}{dx} \text{ , where} \quad (7)$$

J = the diffusion rate (g m^{-2} d^{-1})
ϕ = porosity (m^3 interstitial water/ m^3 wet sediment)
D_x = the diffusion coefficient (in sediment, m^2 d^{-1})
dc = concentration difference between interstitial water and hypolimnion (g m^{-3})
dx = diffusion distance (m).

D_x was estimated according to Clavero et al (1992):

$$D_x = \frac{D_i \phi^3}{1.28} \text{ , where} \quad (8)$$

D_i is the molar diffusion coefficient for H_2PO_4 ($4.08*10^{-5}$ m^2 d^{-1}; Gonsiorczyk et al. 1997). The porosity ϕ was estimated from the composition of the dry sediment according to Sarazin et al. (1995):

$$\phi = \left[1 + \frac{Ws}{2.5(Wt - Ws)}\right]^{-1} \text{ , where} \quad (9)$$

Wt = the total mass of the sediment, and
Ws = the dry mass of the sediment.

0.01 m was used for the diffusion distance dx. To arrive at the concentration gradient dc, the increase in the interstitial water dissolved P concentration upon a dissolved Si pulse (section 3.7.) was estimated with the aid of the calculated Si pulses and the regression equations and related to the hypolimnetic concentration of dissolved P in the respective lake. The

hypolimnion P concentration was measured using the molybdenum blue-ascorbic acid method (Murphy and Riley 1962) from 0.2 µm-filtered samples collected from the lakes in 1995-1999 (VII). Zero-estimates calculated from the unmanipulated P concentration in the sediment interstitial water were included.

3.9. Statistical analyses

In articles I and II the data sets were analysed with ANOVA and a two-sample paired student's t-test (Excel 5.0c. analysis tools package). In articles III and V (sub-experiment with cultured phytoplankton) the effects of the treatments were tested with analysis of variance (ANOVA, SAS release 6.07, SAS Institute Inc. 1992). In the sub-experiment with settled seston (V) analysis of variance with repeated measures (ANOVAR) was used (SAS Institute Inc. 1992). In article IV, the effects of the treatments were tested with ANOVA and Tukey's studentized range test by the GLM procedure of SAS (SAS Institute Inc. 1989). The regression equations in article VII were fitted with the least squares method (Excel 5.0c). Test values of $p<0.05$ were regarded as statistically significant in all cases.

4. Results

4.1. Methodological studies

4.1.1. The impact of freezing on Si analyses

The Si concentrations in the interstitial water samples from May (17 mg l^{-1} Si, Fig. 2A) and November (26 mg l^{-1} Si, Fig. 2B) were lowered to the same level (11 mg l^{-1} Si) by filtering through 0.2 µm or 100 000 dalton membranes. An additional filtering through a 10 000 dalton membrane lowered the Si concentration in the November samples to 8.9 mg l^{-1} Si. All the pre-filtered May-samples contained around 9 mg l^{-1} Si after freezing, while the post-frozen recovery of Si was on the level 6.1 - 7.0 mg l^{-1} Si both in the unfiltered and in the 0.2 µm and 100 000 dalton-filtered November samples. When interstitial water samples were first frozen and only thereafter filtered (0.2 µm), less Si was recovered in AAS-measurable form (4.2 ± 0.7 mg l^{-1} Si) than when they were filtered before freezing (6.8 ± 0.9 mg l^{-1} Si, I).

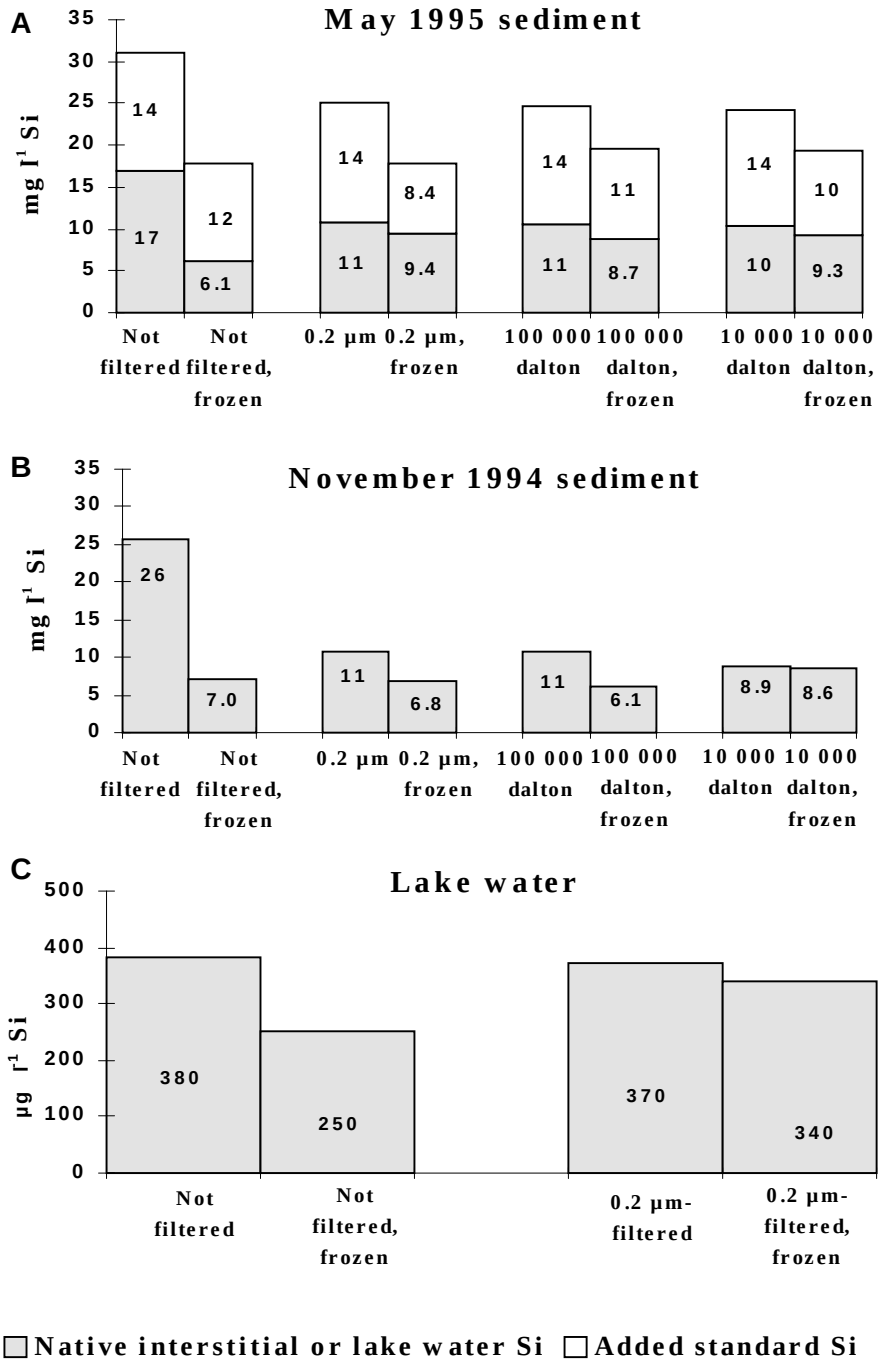


Figure 2. The impact of freezing and filtration on the measurable Si in Lake Vesijärvi interstitial water (A. and B., mg l^{-1}) and lake water (C., µg l^{-1}) samples. The numbers indicate the exact amount of detectable Si. In A., some of the samples were enriched with Si standard solution (I).

The Si in lake water samples was statistically significantly affected by freezing only in the unfiltered samples (Fig. 2C, I). Neither unfiltered nor 0.2 µm-filtered lake water to which Si standard solution had been added lost statistically significant amounts of the added Si when frozen (I). Freezing immobilised part of the added standard solution Si as well when interstitial water samples were enriched with Si standard solution and frozen, regardless of

whether the samples had been filtered or not before freezing (Fig. 2A). If the pH of unfiltered interstitial water samples was lowered below 2 before freezing, the post-frozen Si concentrations were approximately the same as those in the filtered samples (May sediment, I). Filtering pH 2 samples through 0.2 µm membranes before freezing did not alter this result. Some recovery of immobilised Si occurred when thawed samples were left standing for a week at +4°C but the entire pre-frozen amount was not recovered (I).

4.1.2. ^{68}Germanium as a tracer for Si in sediment

The total extractable Si amounted to 11.8 mg g^{-1} Si in both the control and the diatom treatment (II). Most of this Si was sorbed to the Fe- and Al-oxides in the NH_4F and NaOH-extractable fractions (ca 65 %, Fig. 3). Slightly more than 30 % was found in the H_2SO_4-fraction and about 2 % in soluble or easily dissolved (the NH_4Cl-fraction) form (Fig. 3).

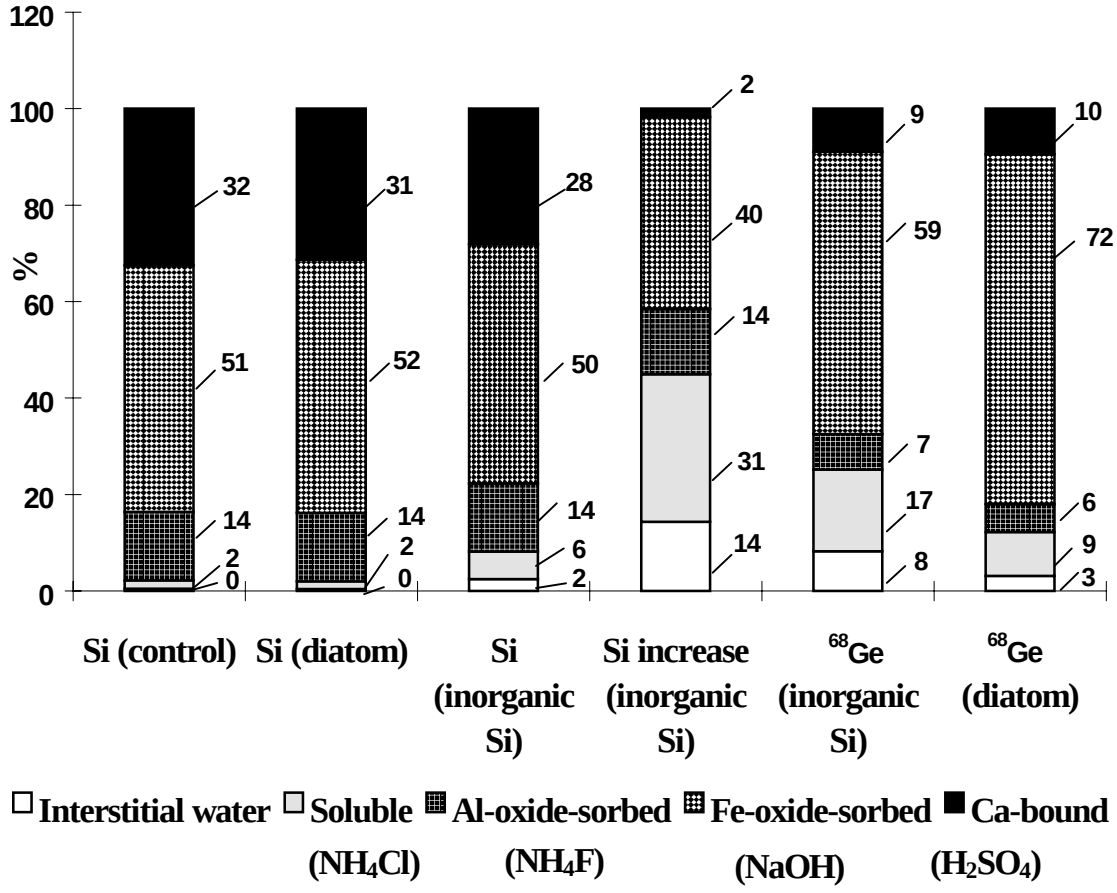


Figure 3. A comparison between the procentual distribution (%) of the total extracted Si, the Si increase induced by the inorganic Si addition (inorganic Si treatment only), and the total extracted ^{68}Ge between five sediment pools in the control (Si data only), diatom and inorganic Si treatments (II). The extractant for each sediment pool is given in parentheses.

In the inorganic Si treatment the total amount of extracted Si was statistically significantly higher (13.7 mg g^{-1} dry sed.) than in the control treatment (II). The increases in extractable Si were statistically significant in the interstitial water and in the NH_4Cl-extractable fraction, but not in the other sediment pools. The extraction procedure recovered 43 % of the added ^{68}Ge in the inorganic Si treatment and 76 % in the diatom treatment (II). The remaining ^{68}Ge-activity was found in the residual sediment (indicated by Geiger-counting after the last extraction).

Most of the total extracted Si in the inorganic Si treatment was found in the NaOH- and H_2SO_4-fractions (Fig. 3). Less than 10 % of the total extracted inorganic Si was found in the interstitial water and in the NH_4Cl-extractable fraction. Compared to this, relatively more of the total recovered ^{68}Ge was found in the interstitial water and in the NH_4Cl-fraction (more than 20 %, Fig. 3), and slightly more in the NaOH-fraction. In the NH_4F- and H_2SO_4-fractions relatively less ^{68}Ge than Si was extracted. If the increase in Si caused by the inorganic Si addition (inorganic Si treatment - control) in each fraction was calculated and the distribution of this Si increment between the fractions studied, the main part (54 %) was found in the NaOH- and NH_4F-fractions. The interstitial water and NH_4Cl-fractions were also important, while the H_2SO_4-fraction was of very minor importance (Fig. 3). In the diatom treatment, markedly less of the overall higher recovery of ^{68}Ge was found in the interstitial water and the NH_4Cl-extractable fraction, but the recovery in the H_2SO_4-fraction (10 %) differed quite little from the inorganic Si treatment. Most of the ^{68}Ge-label was recovered in the NaOH-extractable pool (72 %, Fig. 3).

4.2. The influence of inorganic Si additions on the distribution of P in surface sediment

4.2.1. The P and P+Si dual labelling study

When only P was added, very little ^{33}P and ^{32}P was recovered in the interstitial water and resin-extractable fractions throughout the experiment. The bulk of the added labels were found in the inorganic NaOH-extractable fraction (75 % for ^{33}P and 99 % for ^{32}P), with 1-3 % in the inorganic resin-extractable fraction and less than 0.07 % in inorganic form in the interstitial water (Fig. 4). The recovery in most of the inorganic fractions decreased with time. Three to five percent of the labels were recovered as organic NaOH-extractable P, 0.01-0.02 % in the organic resin fractions and 0.002-0.007 % in organic forms in the interstitial water (III).

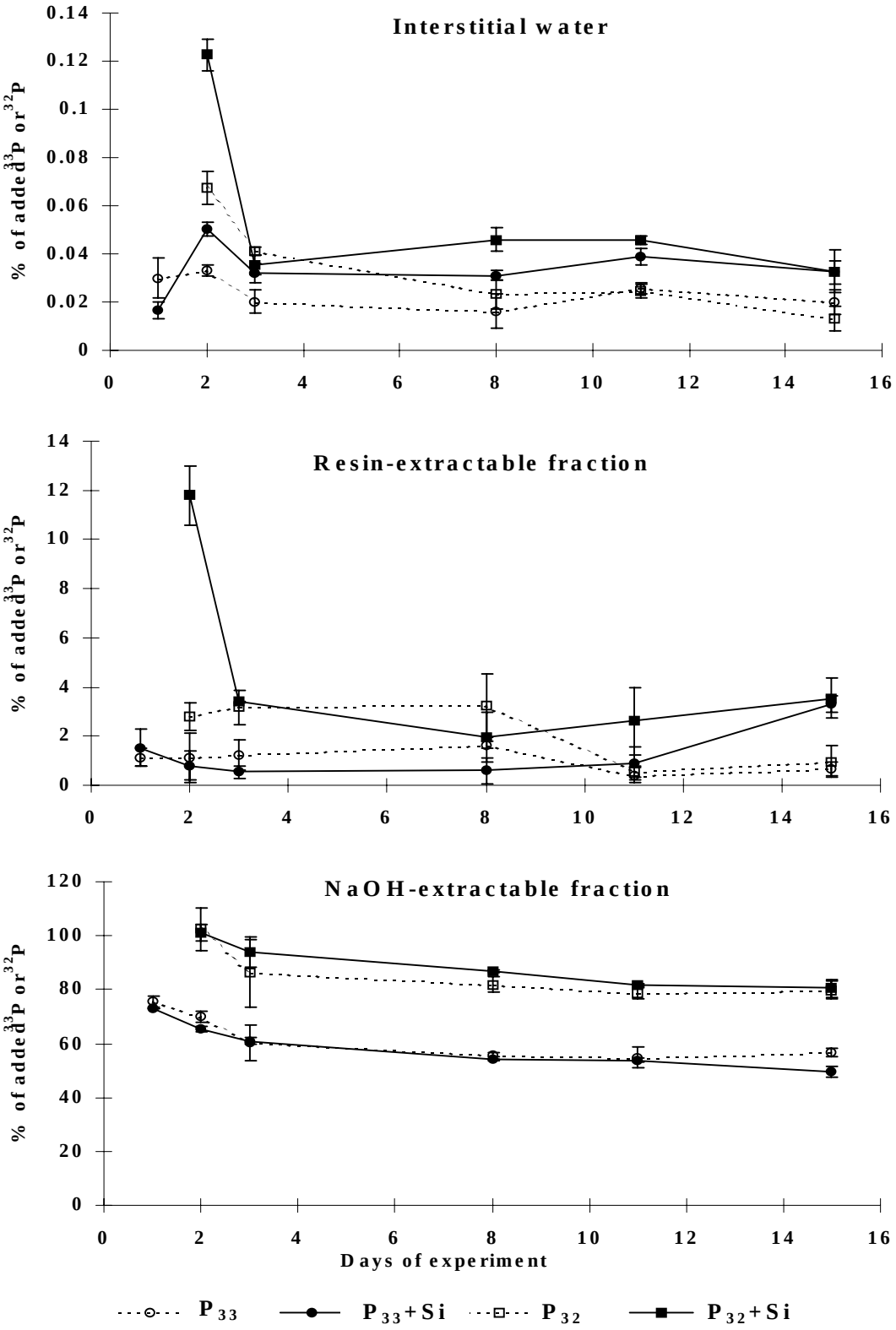


Figure 4. The percentage of the added ^{33}P and ^{32}P-labels recovered in inorganic form in the interstitial water, in the labile fraction extracted by resins, and in the NaOH-extractable fraction (Al- and Fe-oxide-sorbed) from Lake Vesijärvi sediment samples enriched with either P or P+Si (9 mg l^{-1} sed. Si). The ^{33}P-label was added 4 d before and the ^{32}P-label with the enrichments (III).

When P+Si was added, statistically significantly more inorganic ^{32}P and ^{33}P was recovered in the interstitial water throughout the experiment (Fig. 4), and more ^{32}P at the start and end of the experiment in the resin-extractable fraction. A large peak of inorganic ^{32}P in the interstitial water and the resin-fraction occurred on enrichment day. Towards the end of the experiment, the ^{33}P in the inorganic resin-extractable fraction increased in the P+Si samples (III).

4.2.2. The Si, pH and Si+pH fractionation study

In the control samples the NaOH fractionable Fe-bound-P was the largest pool, amounting to 49 % of the total fractionable P reserves (1.4 mg g^{-1}, IV, Fig. 5).

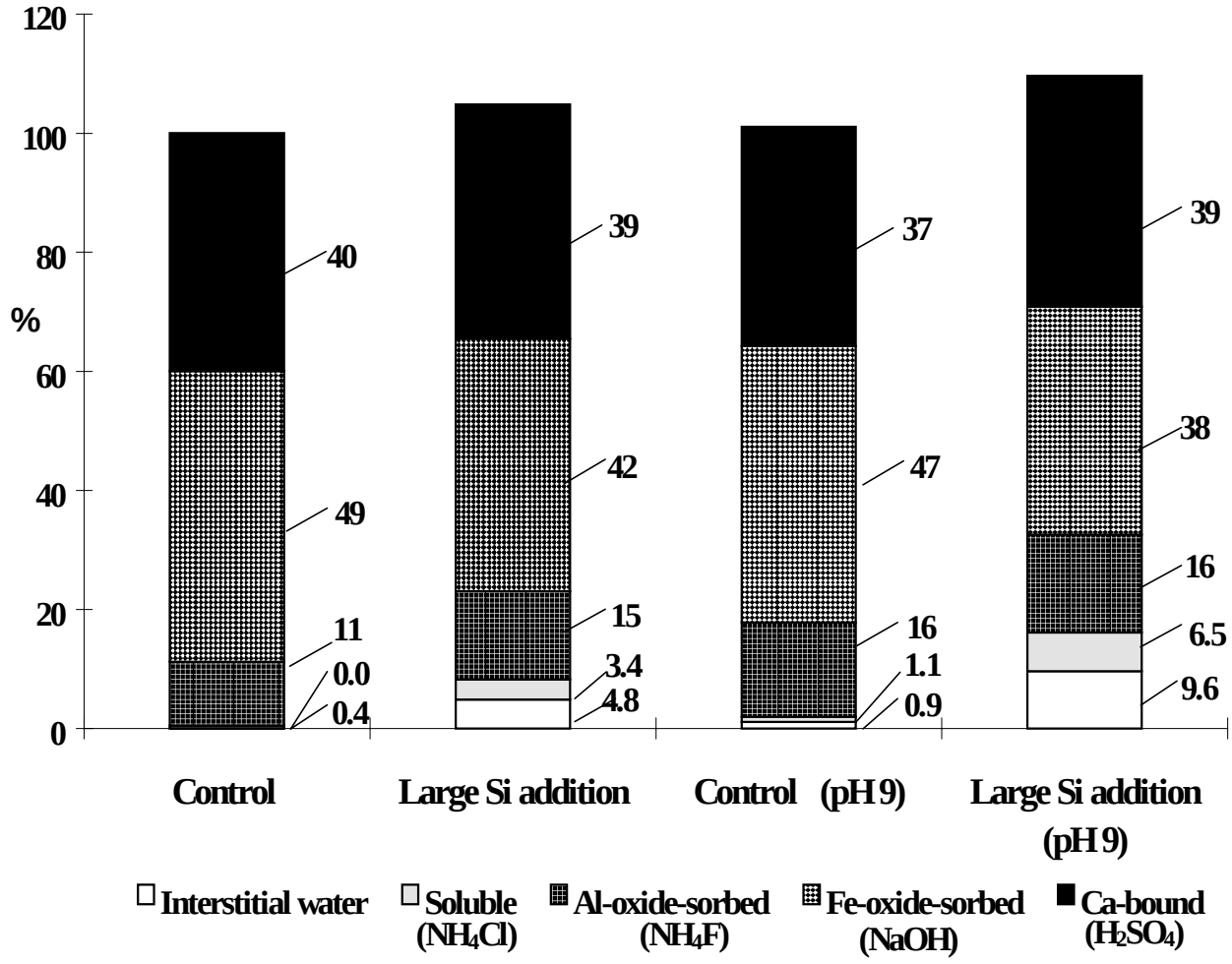


Figure 5. The distribution of P (as % of the total extractable P) between five sediment pools in Lake Vesijärvi sediment samples to which solutions of either distilled water (control) or 940 mg l^{-1} Si (47 mg l^{-1} sed., inorganic Si) had been added at two pH levels (7 and 9; IV). The total exceeds 100 % due to the overlap of the interstitial water and the (NH_4Cl-) soluble pools. The extractant for each sediment pool is given in parentheses. The smaller Si enrichment did not differ from the control (IV).

The second largest P fraction was the H_2SO_4 fraction (Ca-bound P, 40 % of the total P). The proportion of the Al-bound NH_4F fraction was 11 %, and the NH_4Cl- and interstitial water fractions were small (Fig. 5). The high Si enrichment increased the amount of P in the NH_4F fraction by 4 %-units while the P in the NaOH fraction declined clearly (by 7 %-units). The proportion of P recovered in the NH_4Cl fraction increased almost 10 times and that in the interstitial water more than 100 times (Fig. 5); the Si concentration in the interstitial water rose to 6.9 mg l^{-1} (IV). When pH was raised, the amount of P recovered in the NaOH- and H_2SO_4-fractions decreased slightly, increased by 5 %-units in the NH_4F fraction, two-fold in the NH_4Cl fraction and 25-fold in the interstitial water (control pH 9, Fig. 5). The impact of the high Si enrichment on the redistribution of fractionable P was further enhanced at raised pH, most notably as increases in the NH_4Cl fraction and the interstitial water and as a decrease in the NaOH-fraction (Fig. 5).

4.2.3. Different Si additions and lake sediments

When the concentration of P in Lake Vesijärvi sediment interstitial water was studied without any Si addition, the concentration of P decreased during the 44 h experiment period, from 22 to 8 µg l^{-1} (Fig. 6, VII).

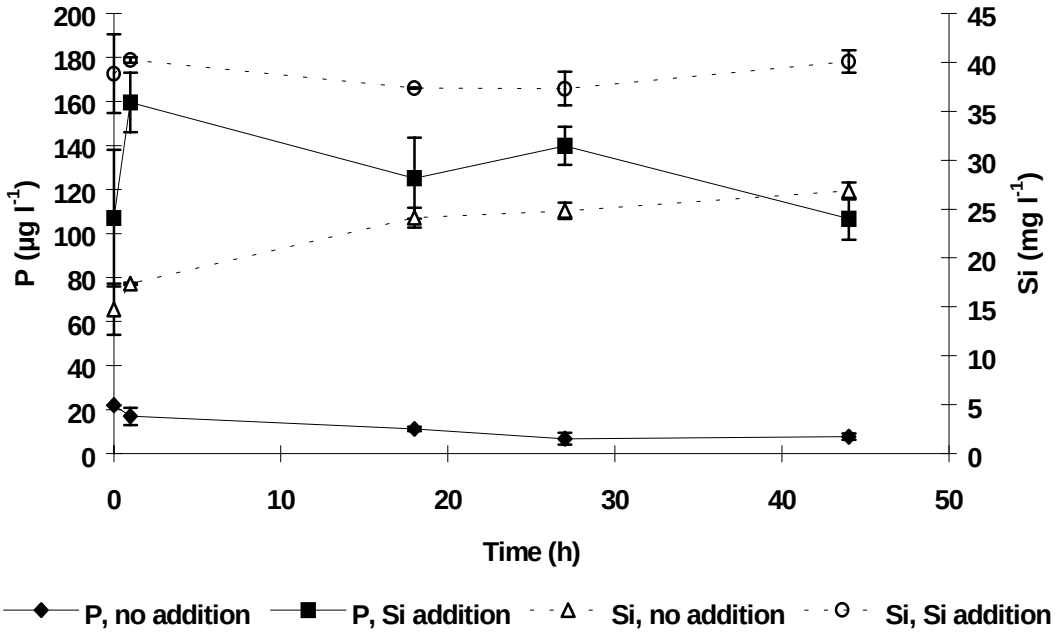


Figure 6. The 44 h-development of the concentration of dissolved P (µg l^{-1}, left-hand scale) and Si (mg l^{-1}, right-hand scale) in the interstitial water of surface sediment samples from Lake Vesijärvi to which solutions containing either no silicate or 800 mg l^{-1} silicate (40 mg l^{-1} sed.) had been added (VII). Standard deviations are shown as vertical lines.

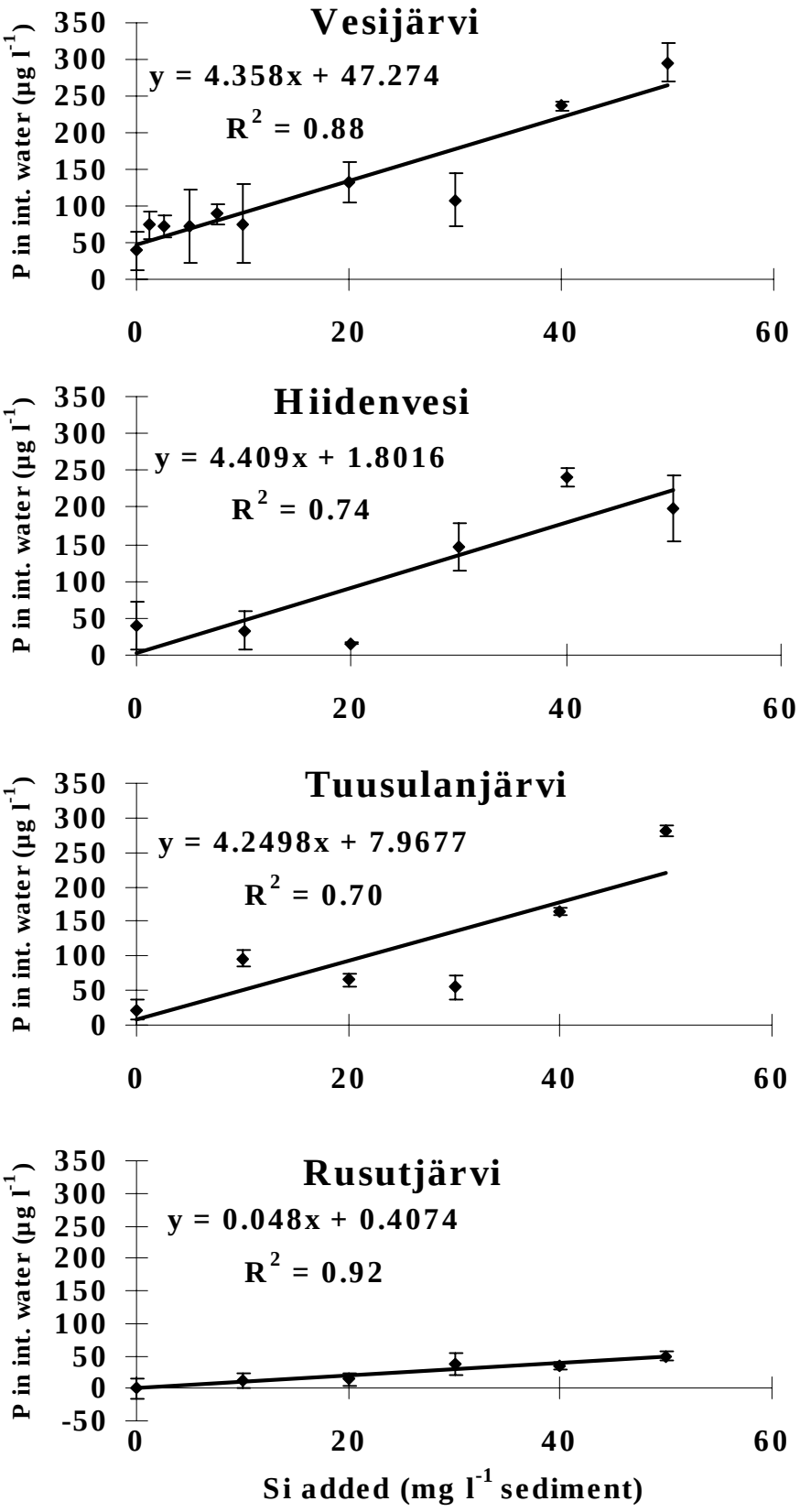


Figure 7. The linear least-square regressions obtained by plotting the dissolved P concentrations of the sediment interstitial water against the added Si concentration (as mg l^{-1} sediment) for sediment from Lake Vesijärvi, Lake Hiidenvesi, Lake Tuusulanjärvi and Lake Rusutjärvi (VII). Standard deviations are shown as vertical lines.

When a Si solution corresponding to 40 mg l^{-1} sed. was added the desorption was immediate; i.e. the P concentration was higher than in the other series immediately after the addition (110 µg l^{-1} at 0 h) and reached a maximum 1 h after the addition (160 µg l^{-1}), whereafter it declined, reaching the initial (110 µg l^{-1}) level again after 44 h. The Si concentration in the interstitial water increased from 15 to 27 mg l^{-1} during the experiment although no Si was added. The Si addition raised the concentration to approximately 40 mg l^{-1} (Fig. 6).

The response to the Si addition varied somewhat among the lakes (Fig. 7). In Lake Vesijärvi, the initial P concentration (40 µg l^{-1}) increased quite linearly (Fig. 7), reaching 130 µg l^{-1} at a Si addition of 20 mg l^{-1} sed. and 300 µg l^{-1} when 50 mg l^{-1} sed. of Si was added; the scatter was however quite high. In Lake Hiidenvesi, the concentration of dissolved P in the interstitial water increased from the initial 40 µg l^{-1} only at Si additions exceeding 20 mg l^{-1} sed., about fourfold (to 240 µg l^{-1}).

In Lake Tuusulanjärvi, the same pattern appeared although the initial P concentration was lower (22 µg l^{-1}) and the highest Si-induced P concentration higher (280 µg l^{-1}). In Lake Rusutjärvi the P concentration in the interstitial water increased linearly from the very low initial concentration to a level much lower than in the other lakes (50 µg l^{-1} at a Si addition of 50 mg l^{-1} sed.). The fit of the least-square linear regression for the Si-induced release of P was best for the data from Lake Vesijärvi and Lake Rusutjärvi (0.88 and 0.94) and poorer for the other lakes (0.70-0.74; Fig. 7).

The Si concentration in the interstitial water increased from 6 mg l^{-1} in Lake Rusutjärvi, 17 mg l^{-1} in Lake Tuusulanjärvi and 11 mg l^{-1} in Lake Hiidenvesi to a level between 20 and 25 mg l^{-1}, where it levelled out (VII). In Lake Vesijärvi the already high Si concentration increased from 21 to 44 mg l^{-1}. The initial pH ranged from 5.7 in Lake Vesijärvi and Lake Rusutjärvi to 6.2 in Lake Tuusulanjärvi and 6.6 in Lake Hiidenvesi (VII). The highest absolute value occurred in the Lake Hiidenvesi samples at the highest Si addition (8.2). In Lake Vesijärvi and Lake Tuusulanjärvi the highest pH values were 6.9 and 7.0, respectively.

4.3. The influence of diatom additions on the availability of P in surface sediment

In the sub-experiment with isotope labels and cultured phytoplankton, the bulk of both the labels (60-90 %) was recovered in the inorganic NaOH-extractable fraction. When live diatoms or cyanobacteria were added, this did not change substantially after the enrichments

on day 2 (Fig. 8). The ^{33}P- and ^{32}P-activities (V) recovered in the interstitial water were very low all through the experiment, and the live enrichments did not differ from each other. Compared to the live samples, the inhibition of bacteria significantly increased the recovery of labelled P in the interstitial water. It also significantly increased the recovery of inorganic NaOH-extractable ^{33}P in both treatments and the recovery of ^{32}P in the cyanobacteria treatment, where the added P was mainly outside the cells (V).

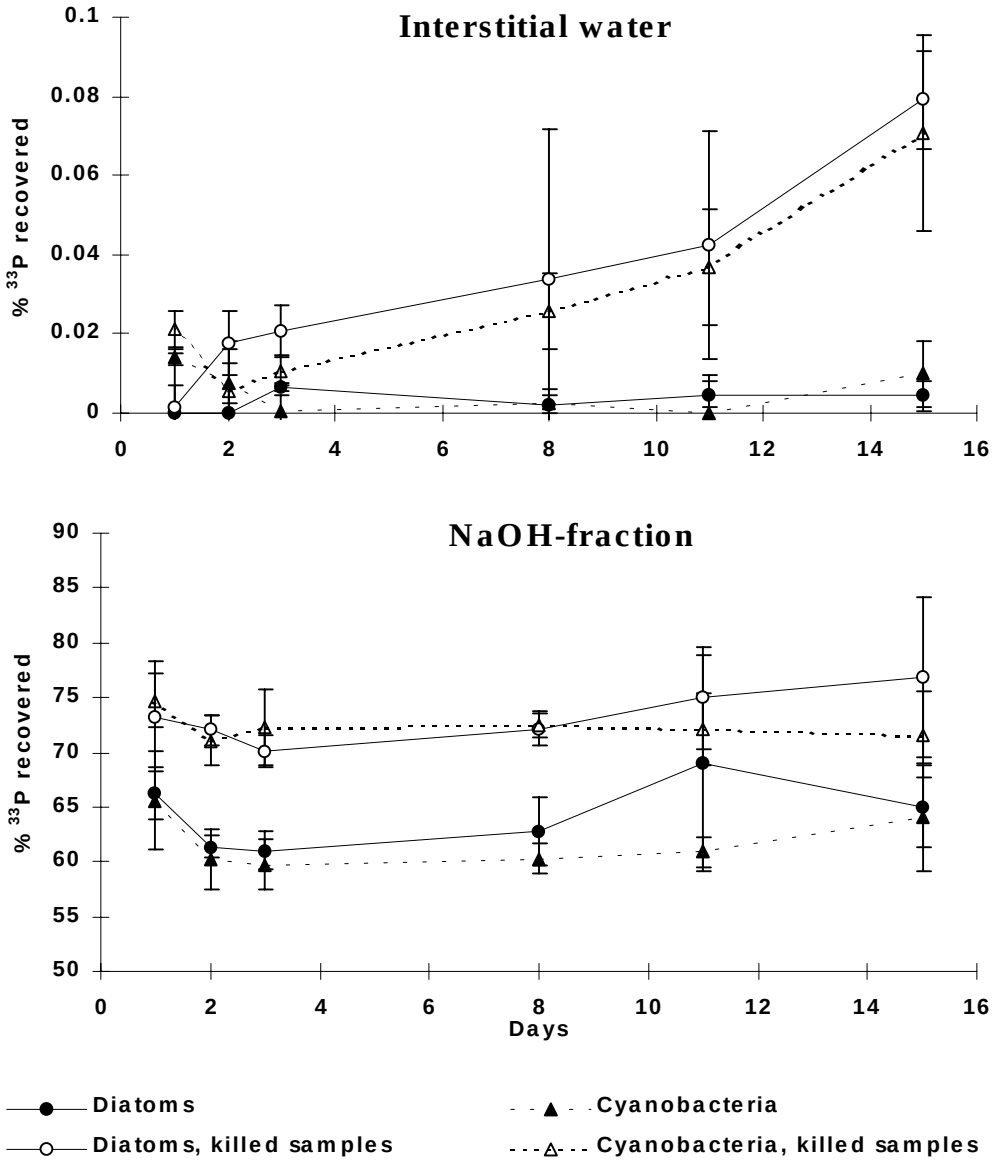


Figure 8. The percentage of the ^{33}P-label recovered in inorganic form in the interstitial water and in the NaOH-extractable fraction (Al- and Fe-oxide sorbed) from Lake Vesijärvi surface sediment samples which had received additions of either cyanobacteria (670 µg l^{-1} chl a) or diatoms (120 µg l^{-1} chl a). In the killed samples bacterial activity was inhibited by addition of formaldehyde to the sediment (final concentration 0.02 %). The ^{33}P-label was added to the sediment 4 d prior to the enrichments (V). Standard deviations are also shown.

In the sub-experiment with settled seston, the mobilisation of P was enhanced only by the May-material: in these samples the concentration of dissolved P in the interstitial water increased to 6.3 µg l^{-1}, while it remained at 1 µg l^{-1} in the control samples (Fig. 9). The other settled materials had no effects on the P release. The May-material also significantly enhanced the leucine uptake. The July-material did not statistically significantly change any of the measured parameters, but the August-material increased the leucine uptake at the end of the experiment.

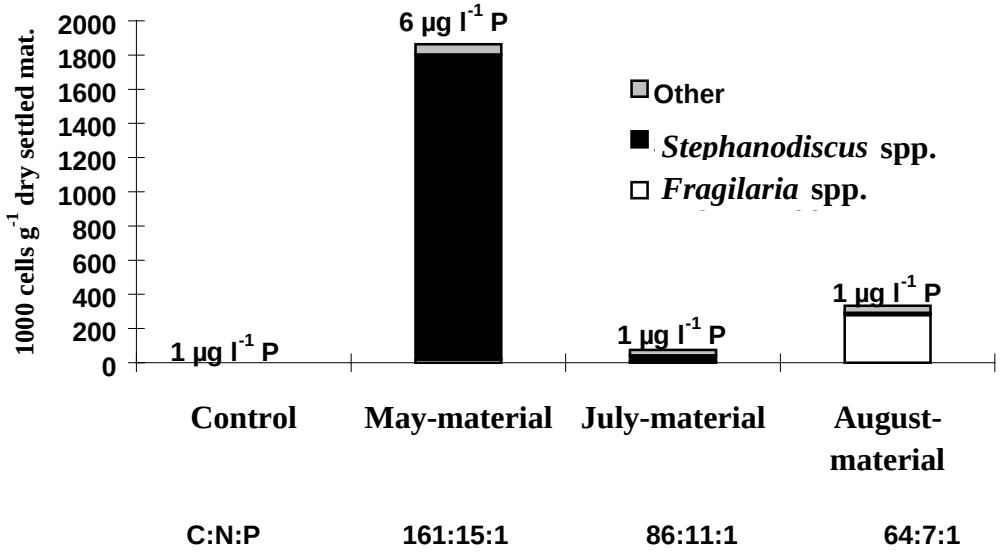
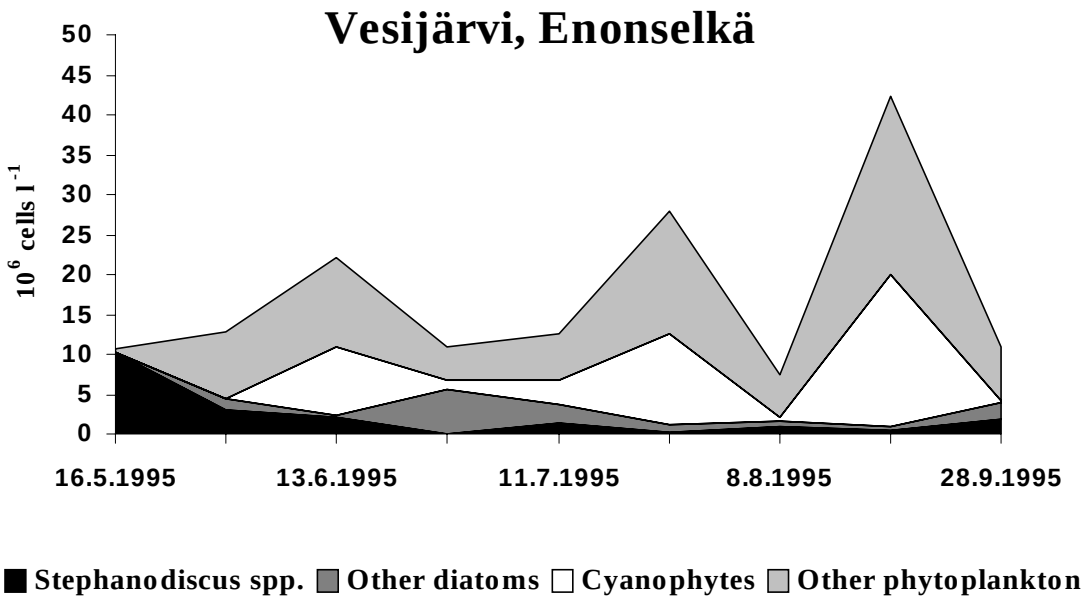


Figure 9. The results from the experiment with settled seston. The concentration of dissolved P in the interstitial water of the sediments enriched with settled seston is shown as numbers on top of the vertical bars. The phytoplankton composition of the settled seston is shown as vertical bars (10^3 cells g^{-1} dry settled material) and the C:N:P ratios of the seston as numbers at the bottom of the figure (V).

4.4. The magnitude of Si dissolution from diatoms at the sediment surface

The total amount of Si present in dissolved form in the water column in Lake Vesijärvi in early 1995 was estimated (VI) to decline from 29 g m^{-2} sed. to 3 g m^{-2}; approximately 1 g m^{-2} of Si was bound to the standing stock of diatoms at that point of time (cf. Fig. 10A, 11). Assuming that all available Si was taken up by diatoms, the maximum of potentially sedimenting diatom-bound Si was estimated as 25 g m^{-2} sediment (25-130 mg l^{-1} sed., depending on the sediment layer depth, VI). The minimum of potentially



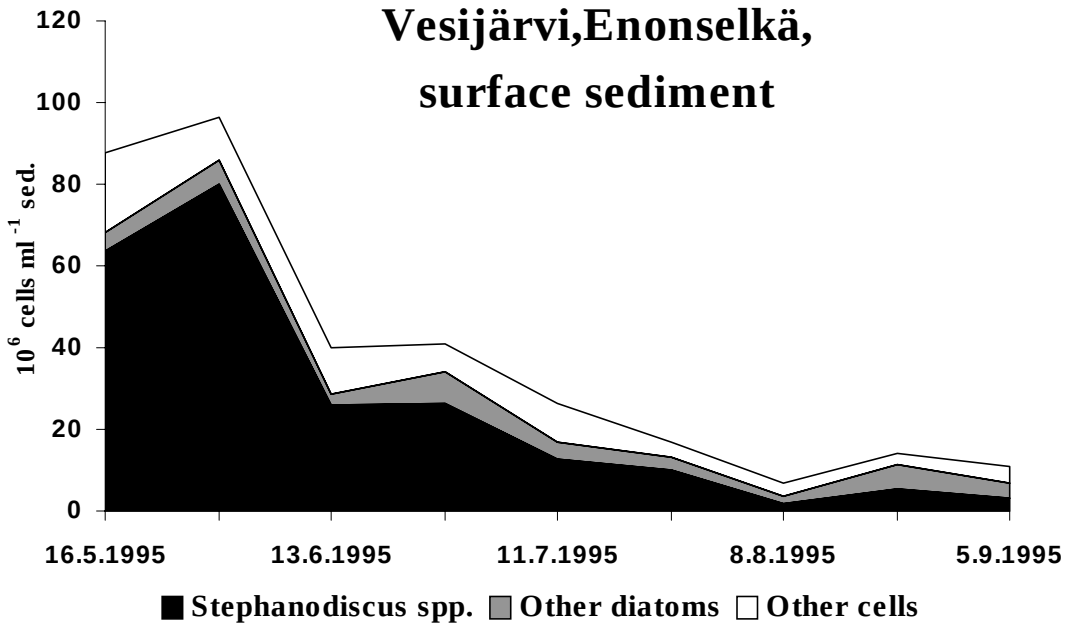


Figure 10 A. The composition of the phytoplankton assemblage (as 10^6 cells l^{-1}) with emphasis on the diatom species composition in the water column of Lake Vesijärvi (Enonselkä, 1995). The phytoplankton cells enumerated from the surface sediment (as 10^6 cells ml^{-1} sed.) during the studied period of time is also shown (VI, VII).

sedimenting, diatom-bound Si was estimated as 2 g m^{-2} sediment (2-8 mg l^{-1} sed., VI). The Si deficit based on the total number of cells in the surface sediment (Fig. 10A) amounted to 21 g m^{-2} sediment (21-110 mg l^{-1} sed.). The highest total Si pulses, where all the diatoms were assumed to dissolve, were maximally as high as 2500 mg l^{-1} sed. (VI).

In article VII, the Si pulse estimate (sediment layer depth 1 cm) based on the water deficit of Si in Lake Vesijärvi in 1995 was re-estimated as 97 mg l^{-1} sed. (Table 1). The water deficit Si pulse estimates for the other lakes were lower, 50 mg l^{-1} sed. for Lake Tuusulanjärvi and 28 mg l^{-1} sed. for Lake Hiidenvesi. The Si pulses calculated from the maximal standing stocks of diatoms were lower and ranged from 0.2 mg l^{-1} sed. (1994) to 14 mg l^{-1} sed. (1995) for Lake Vesijärvi; the average (1982-1995) was 4.5 mg l^{-1} sed. (Table 1). For Lake Hiidenvesi, these Si pulses ranged from 1.3 to 2.3 mg l^{-1} sed. and in Lake Tuusulanjärvi in 1997 the Si pulse calculated from the standing stock of diatoms was 2.1 mg l^{-1} sed. (see Fig. 10B and 11).

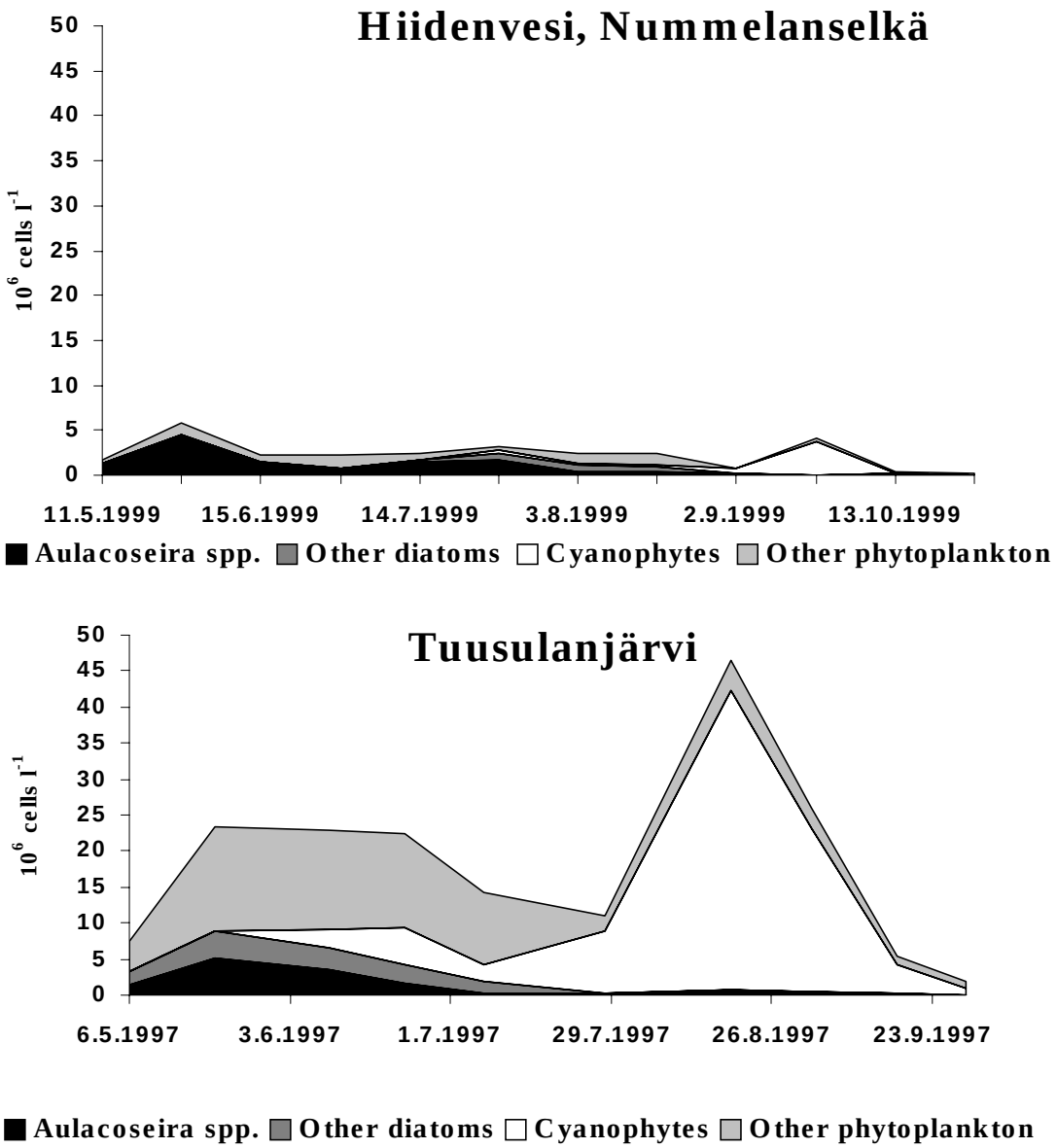


Figure 10 B. The composition of the phytoplankton assemblages (as 10^6 cells l^{-1}) with emphasis on the diatom species composition in the water column of Lake Hiidenvesi (Nummelanselkä, 1999) and Lake Tuusulanjärvi (1997; VII).

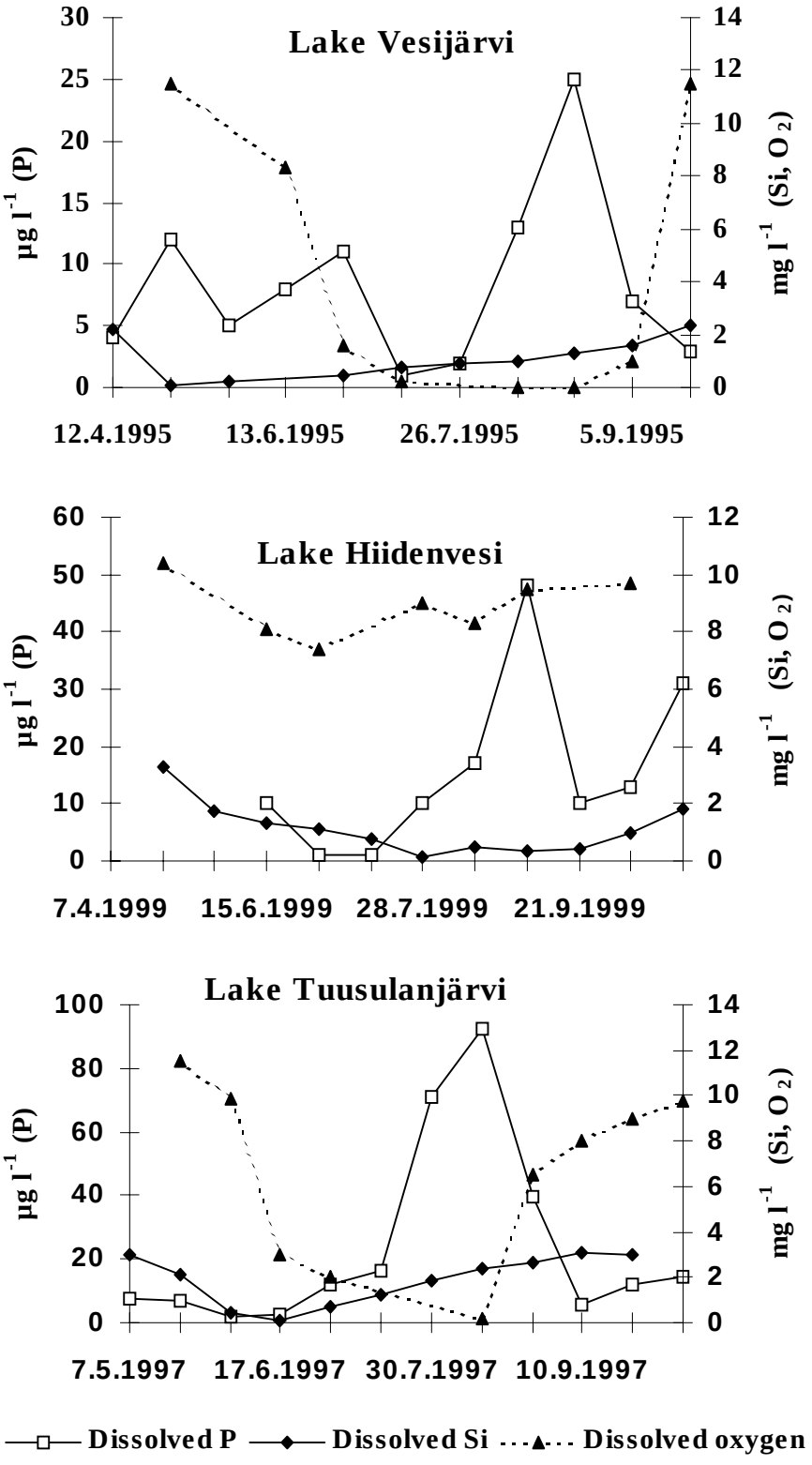


Figure 11. The dissolved silicate (Si, average water column values), phosphate (P, average hypolimnion values (Vesijärvi, Tuusulanjärvi) or 0-2 m values (Hiidenvesi)) and oxygen concentration (mg l^{-1}, hypolimnetic values) in Lake Vesijärvi (1995), Lake Hiidenvesi (1999) and Lake Tuusulanjärvi (1997; VII).

Table 1. Estimated pulses of Si in the sediment surface layer due to the dissolution of spring diatom blooms (VI, VII), and the estimated P loading J caused by these Si pulses and by the measured dissolved P concentration in the interstitial water without any Si addition (No Si pulse) in the examined lakes (VII). The water Si deficit was calculated from the disappearance of dissolved Si from the water column, and the diatom value from the maximal standing stock of diatoms in the surface water. The surface sediment layer thickness was assumed to be 0.01 m and the dissolution rate of the diatom cells 3 % d^{-1} (Lake Hiidenvesi and Lake Tuusulanjärvi) and 5 % d^{-1} (Lake Vesijärvi). The diffusion distance d_x was assumed to be 0.01 m.

	Date	Dominant diatom taxa	Si pulse (mg l^{-1} sed.)	Diss. P in hypolimnion (mg m^{-3})	Diss. P in interstitial water (mg m^{-3})	J (mg m^{-2} d^{-1})
No Si pulse						
Vesijärvi				5	39	0.10
Hiidenvesi				10	40	0.06
Tuusulanjärvi				4	22	0.07
Water deficit maxima						
Vesijärvi	16.5.1995	*Stephanodiscus*	97	5	470	1.35
Hiidenvesi	26.8.1998	*Aulacoseira*	9.5	10	43	0.06
	3.6.1999	*Aulacoseira*	28	10	120	0.21
Tuusulanjärvi	3.6.1997	*Aulacoseira*	50	4	220	0.78
Diatom utilisation maxima						
Vesijärvi max.	16.5.1995	*Stephanodiscus*	14	5	110	0.30
Vesijärvi average (1982-95)			4.5	5	67	0.18
Hiidenvesi max.	21.9.1997	*Aulacoseira*	2.3	10	11	0.00
Hiidenvesi average (1997-9)			1.8	10	10	0.00
Tuusulanjärvi	21.5.1997	*Aulacoseira*	2.1	4	17	0.05

4.5. The impact of the estimated Si dissolution on the mobilisation of P

Using the scenarios for possible Si dissolution pulses in surface sediment in spring presented in section 4.4. and the regression equations between added Si and P released into the interstitial water presented in Fig. 7 (section 4.2.3.), the potential pulses of P into the hypolimnion caused by spring blooms of diatoms were estimated based on Fick's Law (section 3.8.) to range from 0 to 1.35 mg m^{-2} d^{-1} (Table 1). The highest P diffusion rates were calculated for Lake Vesijärvi and Lake Tuusulanjärvi and the lowest for Lake Hiidenvesi, where only those based on the (maximal) Si pulses calculated from the water deficit were substantially higher than zero. The calculated P fluxes without any Si dissolution pulses (based on the P concentration in the interstitial water at zero Si addition) were quite low (Table 1).

5. Discussion

5.1. Methodological aspects of Si analyses in sediment

5.1.1. Freezing-induced Si polymerisation

Although sediment studies are an integral part of limnology, the methodology for e.g. sediment fractionation is to a large extent a sometimes modified, sometimes directly borrowed version of that originally developed for soil analyses (Williams et al. 1971, Hartikainen 1979, Hieltjes and Lijklema 1980). Several aspects of the sediment environment make the direct application of limnological analytical methods - e.g. sampling methodology, nutrient analysis, application of tracer studies - something of a gamble. The sediment differs from the rest of the aquatic environment in that it is a vastly more concentrated and much more heterogeneous environment. The amorphous nature and colloidal chemistry of Si (e.g. Hallmark et al. 1982, Tan 1994) makes sediment research concerned with different forms of Si properties even more intriguing.

This is very well illustrated in the investigation into the disappearance of dissolved Si from the sediment interstitial water (I). The strength of the freezing-induced complexion of Si in the sediment samples was clearly related to aspects of the sediment medium. The most likely explanation for the disappearance of Si during the freezing process was the complexion of Si, mediated by particles, into high-molecular-weight forms not measurable with the spectrophotometrical methods used. Below concentrations of 140 mg Si l^{-1} and at pH values normally found in natural waters (2 - 9) dissolved Si appears as monosilicic acid, which is capable of forming complexes with e.g. soil organic compounds (e.g. Tan 1994). Tessenow (1966) and Burton et al. (1970) have showed that some colloidal suspensions and Si polymers of high molecular weight cannot be detected by spectrophotometrical methods. Freezing seems to initiate the complexion or polymerisation of Si, which has also been shown to take place at very high concentrations (>140 mg l^{-1}) and when dehydration takes place (Tan 1994). Presumably the molecules remaining in solution are concentrated as the water in the sample is frozen, and this stimulates complexion.

Since the disappearance of Si was much more marked in the sediment interstitial water than in the more dilute lake water, the high incidence of particulate material was probably important for the phenomenon. Our experiments could only roughly point out the size-range

of the particulate or colloidal material which was responsible for the complexion, however (10 000 - 100 000 dalton-sized molecules). Since these particles were capable of immobilising both sediment-derived and added, extraneous Si, the process was related to the other constituents of the sediment and not primarily to the form of the native Si.

It is not clear to what extent the complexion of Si through freezing may occur in nature, e.g. in shallow, littoral sediments or in water. Nor is it evident whether the process may have any ecological significance. Some polymerised colloidal Si can be utilised by algae (Tessenow 1966), and no consistent data on the reversibility of the complexion process (i.e. on the stability of the complexes formed, Burton et al. 1970, MacDonald and McLaughlin 1982, Aston 1983) exists. The ecological relevance of the freezing-immobilisation of Si is, thus, an interesting question, which merits further study. Further, although the fact that Si samples should not be frozen has been known for decades (Strickland and Parsons 1972, MacDonald and McLaughlin 1982) the storage by freezing of all nutrient samples is still unfortunately common practice in some laboratories, and an additional warning against it is warranted.

5.1.2. ^{68}Germanium as a tracer for Si

Another difficulty which is encountered in sediment analyses concerned with Si is the sheer difficulty of numbers. Tracking down the fate of an addition of Si to surface sediment by quantitative analyses is difficult due to the previous presence of large amounts of different forms of Si. In order to produce a measurable increase in the concentration of Si per g of dry sediment, the amount of inorganic Si added in the ^{68}Ge-labelling experiment (II) had to be very large. Although the solution used in the Si treatment was strong (940 mg l^{-1}) it corresponded to only 0.49 mg g^{-1} Si dry sed., which is only 4 % of all the Si that was extracted by the fractionation procedure from the unmanipulated samples. Consequently, it was difficult to reliably evaluate the distribution of the added Si, since the Si addition caused statistically significant increases in the Si concentrations only in the interstitial water and the NH_4Cl-extractable fraction. As the NH_4F- and NaOH-fractions represent the Al- and Fe-oxides of interest in the sorption competition with P (e.g. Hingston et al. 1967) this diminishes the value of the results. The possibilities of tracking the pathway of Si dissolving from small amounts of diatoms in surface sediment is even more difficult: the quantity of Si in the diatom treatment in the present study was plainly too small to be detected in the Si results.

Radioisotope labelling has been successfully employed in a number of studies concerned with the movement of elements in sediment, most notably with P (e.g. Istvánovics 1993, III, V). The ^{68}Ge isotope has been used quite extensively in biological studies to trace the biological pathway of Si in e.g. diatom metabolism (Azam et al. 1973, Azam 1974, Rivkin 1986). Ge is taken up by Si-utilising organisms such as diatoms as if it were a very heavy, stable Si-isotope (Froelich and Andrae 1981, Froelich et al. 1985). Although no studies were available where the ^{68}Ge label had been used in sediment, the fact that Ge also can replace Si in the lattices of minerals and that it mimics the much more common element Si in many geological processes (Froelich et al. 1985, Kolodny and Halicz 1988) suggested that it might be applied. The ^{68}Ge label was thus tried as a means of tracing the whereabouts of both a large inorganic Si addition and the Si dissolving from comparatively small amounts of diatom cells in surface sediment.

The ^{68}Ge-label posed some initial difficulties, since the label ($^{68}GeCl_4$ in 0.5 M HCl) contrary to expectations was only partially hydrolysed: the presupposition was that, like elemental Ge, $GeCl_4$ would be rapidly hydrolysed into anionic $Ge(OH)_4$ and, when added to an alkaline solution of deionized water and $NaSiO_3 \cdot 9H_2O$, would produce a solution of $Si(OH)_4$ with a trace amount of $^{68}Ge(OH)_4$ (Rivkin 1986). However, only 43 % (inorganic Si treatment) to 76 % (diatom treatment) of the label followed this reaction pattern; the remaining 47-24 % remained in cationic $GeCl_4$-form or precipitated as giant oxide structures of GeO_2 (e.g. Lister and Renshaw 1991). In the sediment the $GeCl_4$-form of ^{68}Ge (the cation $^{68}Ge^{4+}$) was however bound to the oxide surfaces by the specific cation exchange mechanism (Kinniburgh 1982). Neither the giant oxides nor the cationic ^{68}Ge should have participated in the ligand exchange reactions studied or been extracted by the alkaline stages of the fractionation procedure, since the specific cation adsorption is positively correlated with pH (Kinniburgh 1982). Due to these discrepancies the ^{68}Ge results are evaluated as % of the total recovered ^{68}Ge.

The distributions of the extracted ^{68}Ge, the total extracted Si, and the increase in Si caused by the inorganic Si addition were reasonably similar. The added $^{68}Ge(OH)_4$ was rapidly distributed throughout the sediment, occupying the same fractions (sorption sites) as, particularly, the increase in Si caused by the Si addition. Compared to the total extracted Si the distribution of ^{68}Ge was skewed towards the interstitial water, while relatively more of the total extracted Si was found on the Al-oxides. Since the ^{68}Ge describes the distribution of a recent Si addition, while the distribution of the total extracted Si represents the stable state of the sediment where second-phase sorption mechanisms have taken place (House et al. 1998),

this is natural. The retention mechanisms involved for Si are apparently similar to the sorption pattern of P: an initial quick ligand-exchange on the oxide surfaces, followed by slow diffusion into particles (Barrow 1985, Torrent et al. 1992, House et al. 1998). Previous investigations into the behaviour of added Si in soil (Beckwith and Reeve, 1963, Miller 1967) and sediment (Mortimer 1941, 1942, III) have indeed mostly indicated rapid sorption reactions.

Based on the distribution of the recovered ^{68}Ge a large Si addition to surface sediment would, thus, be largely adsorbed to the Fe- and to a lesser extent Al-oxides, with 10-40 % remaining in dissolved or very loosely adsorbed form. As there is, however, evidence both for (Mortlock and Froelich 1987, Murnane and Stallard 1990) and against (Chillrud et al. 1994) preferential adsorption of Ge over Si onto hydroxide surfaces, some caution is advised when interpreting the results. Overall, the use of ^{68}Ge (as $^{68}Ge(OH)_4$!) as a tracer for inorganic Si additions in oxic surface sediment is, however, a viable option, but the chemical speciation of the label should be ascertained before addition to the sediment. The increased sensitivity of the analysis would render such overlarge Si additions as here used unnecessary, and thus minimise the errors caused by e.g. increases in pH.

Although the ^{68}Ge-labelling of the diatoms was quite successful, and the hydrolysed $^{68}Ge(OH)_4$ was incorporated into the diatom frustules, the diatom experiment was, however, not very successful. It was impossible to follow the path of the Si dissolving from the diatoms beyond the interstitial water and the most labile (NH_4Cl and NH_4F-extractable) fractions, since alkaline digestants such as NaOH and Na_2CO_3 are used as extractants in analytical methods for biogenic Si (DeMaster 1981, University of Lund 1982, Conley 1998), and the NaOH-extractant thus dissolved the diatom shells and freed ^{68}Ge and Si from the diatoms and not only the Fe-oxide-adsorbed Si and ^{68}Ge. Although the quite high recovery of ^{68}Ge in the interstitial water and the NH_4F-fraction tentatively indicate high dissolution rates for the small diatom cells, we are unable to ascertain much about the adsorption of ^{68}Ge-labelled $Si(OH)_4$ freed by dissolution to Fe-oxides, and since the Fe-oxides are very important sites for the presumed Si-P sorption interactions, this is a grave error. Thus, ^{68}Ge is not suitable for estimating the fate of Si dissolving from diatoms in surface sediment, although it can be readily used to examine other aspects of diatom metabolism in other environments.

5.2. The influence of inorganic Si additions on the distribution of P in surface sediment

The results from the laboratory experiments (III, IV, VII) clearly indicate that Si is capable of influencing the labile P content of surface sediment under laboratory conditions. Although it is a fact that the silicate and phosphate anions are similar enough to occupy the same ligand exchange sites at particle surfaces (Bohn et al. 1985), the phenomenon is not widely known in limnology (see however Brinkman 1993, Hartikainen et al. 1996). Since the ability of silicate to outcompete phosphate for sorption sites has been applied in soil science to enhance the availability of P in agricultural soil (e.g. Obihara and Russell 1972, Faria et al. 1987, Ma and Takahashi 1991), there is, however, sufficient empirical and experimental data on the phenomenon to substantiate the theoretical possibility of Si-P interactions. Very little experimental work with sediments had however been done (Mortimer 1941, 1942, Rippey 1977, Brinkman 1993, Hartikainen et al. 1996), and the process of desorption and the factors affecting it (e.g. pH) were only sketchily known. The implications of the phenomenon for eutrophicated lakes, where release of sediment-bound P is far from desirable, had not been examined either. In particular, the connection of the Si-P interactions at the sediment surface to the biological cycle of Si had not previously been made. The sedimentation of diatom blooms are in general regarded as a sink, not a potential source, of nutrients (e.g. Smetacek 1984, 1985, Skjoldal and Wassmann 1986).

5.2.1. The sorption process

It was, however, quite easy to show that the addition of a comparatively large amount of Si produces an increase in the concentration of labile P in surface sediment in a short time; i.e. in a manner characteristic of desorption (III, IV). The sorption and desorption of P onto and from sediment particles is a complex process (cf. Carritt & Goodgal 1954, Hingston et al. 1967, House et al. 1998): a rapid (ligand exchange) process is followed by a slower, less well described stage. The secondary stage, which depends on the type of sediment involved, is caused either by a slower diffusion of P into mineral lattices or by reactions with organic material (Barrow 1985**,** House et al. 1998). A true equilibrium may not be achieved for several days (Froelich 1988, House et al. 1995). In article VII, the concentration of P was immediately after the Si addition higher than in the control samples and increased further for 1 h after the Si addition, but declined thereafter for the duration of the 44 h incubation period: the Si-induced desorption of P was apparently partially reversed by time, as the desorbed P with time diffused to less accessible sorption sites. In article III, where the available P in the

interstitial water was followed for a period of 15 days, more or less the same pattern appeared; at the end of the 15 days, more P was recovered in the interstitial water than before the addition but less than at the peak of the desorption; a tentative equilibrium was established after three days. The reaction thus followed a pattern very indicative of Si-induced desorption.

5.2.2. The influence of pH

The competition for sorption sites by silicate and phosphate is clearly influenced by pH, since the pK_a value of silicic acid (9.7) is higher than that of orthophosphoric acid (7.2), and the dissociation into anionic form and competitiveness of silicic acid consequently increases at higher pH (Brinkman 1993). While Si thus can outcompete P for sorption sites when pH reaches approximately 9, this is a quite rare occurrence at the sediment surface under natural conditions in typical boreal freshwater lakes. It is, however, also known that all the sorption sites at an oxide surface will not be occupied by phosphate or silicate alone, but most likely by a combination of the ions. The sorption capacity of an oxide surface is also heavily influenced by the adsorption of the ions themselves and the consequent changes in e.g. plane potential (Brinkman 1993). A sudden high pulse of Si may thus induce desorption of P at lower pH as well (IV).

When measuring the Si-induced increase in desorption of P, pH is also a complicating factor, since raising pH also causes desorption of P by the same mechanism (i.e. by producing P-desorbing OH^--anions, Lijklema 1977, Boström et al. 1982). The two processes may be difficult to separate, particularly as large Si additions easily increase the pH of the sediment slightly, as was shown in the experiments in articles II, IV and VII. Silicate does, however, as shown in article IV, cause desorption of P which is not primarily related to the rise in pH. This was shown both by the different size of the P desorption *and* by the differences in the distribution of P between the sediment fractions when an addition of Si and a raise in pH were compared (see next section). The positive synergistic effects on the desorption of P when pH was raised and Si added (IV) were most likely caused by the increased dissociation of silicic acid at high pH as described above and by some dissolution of biogenic Si. The dissolution of biogenic Si increases as a function of pH (e.g. Lewin 1961, V), and since the concentration of biogenic Si in the studied sediment was quite high (25-28 mg g^{-1} dry sed., Hartikainen et al. 1996), the released Si may have further accelerated the competitive desorption of P.

5.2.3. The reaction sites

The most interesting fact gained from the comparison between the desorption of P caused by high pH and Si (IV) was concerned with the distribution of P between the different fractions, i.e. with the source of the desorbed P. Both high pH and added Si primarily caused desorption of P from the Fe-oxides represented by the NaOH-fraction, but the resorption of P onto the Al-oxides (the NH_4F-fraction) was higher at high pH than when Si was added. Consequently, the Si addition was more efficient at increasing the labile P in the interstitial water. The importance of the Al-oxides as a controlling factor for the soluble P in soils has been demonstrated earlier (Hartikainen 1982), and although the Fe-bound P often is the largest P pool, its role as a P source may be dependent on the resorption of P into Al-bound forms. Si apparently prevents the resorption of the P released from the Fe-oxides by occupying the Al-sorption sites itself. Further support for this hypothesis was provided by the dual-labelling experiment (III), where the effect of a simultaneous addition of P and Si was studied in an experimental set-up where the distribution of both the co-added P and the sedimentary P already present could be closely followed. There, Si was more efficient at reducing sorption of the co-added P than at enhancing desorption of the sedimentary P, and the ability to outcompete P for Al-oxide sorption sites would be a plausible explanation.

The results from article VII also indicated that the proportion between available sorption sites at Fe- respectively Al-oxides may help to determine the impact of a Si addition. In Lake Hiidenvesi and Lake Tuusulanjärvi, the ratio between Fe- and Al-oxides was lower than in the other studied lakes. In these lake sediments, small additions of Si produced no increase in labile P in the interstitial water, and only after a threshold value of Si was reached did any desorption take place, as would be expected if the resorption capacity of the sediment was high due to a relatively higher content of Al-oxides.

In Lake Vesijärvi and Lake Rusutjärvi, where the Fe-oxides were relatively more important, the desorption was closer to linear. Here, the importance of the P reserves adsorbed to the Fe-oxides was evident (see Redshaw et al. 1990): the desorption was much higher in Lake Vesijärvi, where the NaOH-P-fraction was high. The largest Si addition caused surprisingly similar maximal desorption of P from the sediments of Lake Vesijärvi, Lake Hiidenvesi and Lake Tuusulanjärvi, however, despite the differences in the respective concentrations of oxides and adsorbed P, and further studies on the Si-induced desorption of P are obviously necessary.

5.3. The influence of biogenic Si additions on the distribution of P in surface sediment

Small additions of Si in diatom form did not have any discernible influence on the distribution of P in surface sediment (II, V), nor was it as described above (section 5.1.2.) possible to reliably follow the distribution of ^{68}Ge-labelled Si dissolving from diatoms in surface sediment (II). In article V the diatom enrichment was evidently only too small, since it amounted to only 5 % of the daily sedimentation flux (as chlorophyll *a*) in Lake Vesijärvi in May (Koski-Vähälä et al. 2000). Here, the problematic organic nature of diatom cells was demonstrated, since the viability of the diatom and cyanobacterial cells was the main factor determining the impact on the distribution of P (V).

The influence of settled material rich in diatoms was, however, together with the other evidence about Si-induced chemical desorption of P, supportive of our theory (V). Since the May material, which caused release of P, mainly differed from the other materials, which did not, in that it contained more small, easily degradable diatoms, the diatoms were the most likely source of the observed increase of labile P in the interstitial water. Although some of this release may have been due to the P contained in the diatoms and the settled material themselves, as the bacterial activity of the May-material was slightly higher than that of the other materials, the high C:P ratio of the material indicated that the bacteria suffered from a shortage of P. Little release of P through mineralisation would thus have been expected (Goldman et al. 1987, Tezuka 1990). In the other materials the low C:P ratios would, in fact, have been favourable for P release, but apparently any small amounts of released P were adsorbed to the abundant Fe, Al and Mn oxides in the Lake Vesijärvi sediment. The time scales used should have been adequate to detect changes in labile P in the interstitial water, since other experiments have shown that P-release was immediate after enrichment of sediment with organic matter (Andersen and Jensen 1992, Slomp et al. 1993).

Recent experiments have provided new evidence that the degradation of diatom frustules to a larger extent than previously believed is aided by bacteria (Bidle and Azam 1999, but see also Lauwers and Heinen 1974). The bacteria apparently aid the dissolution mainly by degrading the protective organic coating on the cell walls through hydrolytic enzymes (Smith et al. 1992, Bidle and Azam 1999), but it has also been suggested that the proteolytic activities involved produce micro-environments with pH high enough to aid chemical dissolution (Spencer 1983). The increased bacterial activity may thus have further aided the solubilisation of Si from the small centric diatoms (*Stephanodiscus* spp.) in the May-material. Larger diatom

species, such as *Fragilaria* and *Diatoma* spp. in the July- and the August-materials are, on the other hand, dissolved comparatively more slowly (Jørgensen 1955, Sommer 1988). Particle size is, namely, important for the solubility of silica compounds, since the better dispersion of particles (by biological activity) has been shown to increase even the solubility of quartz compounds (Lauwers and Heinen 1974). Also, the surface area: volume ratio strongly influenced the dissolution of different diatoms in an experiment by Barker et al. (1994).

The dissolution rate of the small centric *Stephanodiscus* spp. cells estimated from the disappearance of cells from the surface sediment of Lake Vesijärvi in 1995 (VI) was quite high (5 % d^{-1}) compared to the estimates for freshwater diatoms provided by Sommer (1988). There, the data of Bailey-Watts (1976) and Parker et al. (1977) was recalculated based on a logarithmic model for marine species by Kamatani and Riley (1979), providing estimates of 50 % dissolution after 23 and 58 d, respectively (ca 3 % d^{-1} and 1% d^{-1}). However, since the *Stephanodiscus* spp. cells are very small and known to potentially dissolve quickly (cf. Sommer 1984, 1988), although exact data is not available, the 5 % d^{-1} estimate seems reasonable. The results from the ^{68}Ge-labelling experiment, although somewhat uncertain, also indicated high dissolution rates for the *Stephanodiscus hantzschii* cells used (II). Exact estimates of *in situ* dissolution rates are impossible to obtain in laboratory experiments due to the complicated dissolution process which depends on just about everything, e.g. on the diatom species and its degree of silification (Lewin 1961, Werner 1976), on the pH, temperature and bacterial activity at the sediment surface (Jørgensen 1955, Lewin 1961, Kamatani 1982, Bidle and Azam 1999), and on the interactions with organic and inorganic compounds such as salts (Lewin 1961, Kamatani 1971, Willén 1991, Barker et al. 1994).

5.4. The magnitude of Si dissolution from diatoms at the sediment surface and the impacts on the mobilisation of P and the food web of eutrophicated lakes

The potential importance of the sorption of Si onto and concomitant mobilisation of P from sorption sites in surface sediment lies in the further release of the P into the water column and the magnitude of this flux. The internal loading of P from the sediment into the water is a typical problem in culturally eutrophicated lakes, where the external loading of nutrients has been diminished, but no lowering of the trophic status of the lake achieved due to the mobilisation of large P reserves from the sediment (e.g. Wollenveider 1975, Sas 1989). The accumulation of large sedimentary reserves of P (in non-calcareous lakes) is frequently connected to a high content of Fe, Mn, and Al (e.g. Boström et al. 1982). In most cases, significant release of P from the sediment occurs mainly under anaerobic conditions

(reduction of Fe(III) to Fe(II), whereby solution phase Fe and P increase; Mortimer, 1941, 1942), but it has also been shown that aerobic processes such as an increase in pH can mobilise significant amounts of P (e.g. Lijklema 1977, Ryding and Forsberg 1977, Boström et al. 1982, Jacoby et al. 1982). This study suggests that large pulses of Si is another factor capable of inducing mobilisation of P in the surface sediment layer (III, IV, V, VII) of a magnitude high enough to cause diffusive release into the hypolimnion (VII). The amount of P available for desorption and the structure of the food web that allows for high spring blooms of suitable diatoms, and thus produce high calculated Si pulses, were, overall, responsible for the differences between the calculated Si-induced P fluxes in the studied lakes (VII).

This study does not clarify whether these factors, i.e. the high content of Fe-bound P in the sediment and the aspects of the Si cycle which produces high potential Si pulses to the sediment surface, may be related to each other. The potential for high Si pulses is mainly connected to the composition and intensity of the spring bloom, which are difficult to connect to the high content of sorption sites and P in the sediment. However, the concept of a mismatch between the pelagic and the benthic systems as a cause for high sedimentation pulses has been extensively studied, mainly in marine ecosystems (e.g. Wassmann 1998), where increases in surface water Si even have been shown to directly increase the sedimentation flux (Wassmann et al. 1997). The high P content of the sediment in e.g. Lake Vesijärvi may thus be connected to the intensive diatom spring blooms, if these despite the potential Si-induced desorption of P still sometimes act as semi-permanent sinks for P.

The estimates of P release from the sediment into the water column in freshwater lakes range from 0.2 to 160 mg m^{-2} d^{-1} according to Wisniewski (1991; in House et al. 1998), and the net aerobic release has been estimated to be in the range 0.5 -5 mg m^{-2} d^{-1} (Drake and Heaney 1987). Our maximal estimates for Si-induced fluxes of P (0.2-1.4 mg m^{-2} d^{-1}, VII) fall within the lower half of this range, and were clearly higher than the P release calculated based on the unmanipulated P concentrations in the interstitial water. Experiments with different sediment samples do, however, point to high variability between different batches of sediment. Substituting the values for the interstitial water concentration of dissolved P in Lake Vesijärvi obtained in article V (1 µg l^{-1}) into the P flux model would have produced negative P fluxes for undisturbed Lake Vesijärvi sediments. However, if the results on Si-induced desorption of P from article IV (section 4.2.2.) were used to estimate the Si-induced loading of P, the maximal P fluxes for Lake Vesijärvi would have been in the order of 40 mg m^{-2} d^{-1}.

Although anoxic conditions at the sediment surface may release more P than competition by Si (up to 160 mg m^{-2} d^{-1}, e.g. House et al. 1998), as can also be seen from the correlation between hypolimnetic concentrations of dissolved P and oxygen in Fig. 11, the contribution of Si-induced release of P to the total internal P flux from the sediments in the studied lakes may be high due to the large sediment areas affected. At least in Lake Vesijärvi and Lake Hiidenvesi only small areas of the sediment in the very deeps of the lakes currently suffer from anoxic conditions in the summertime (Tallberg et al. 1999, Koski-Vähälä et al. 2000). Of the Enonselkä basin of Lake Vesijärvi, 83 % is less than 10 m deep (Keto 1973), and the shallow, nonstratifying areas of Lake Hiidenvesi (an estimated 70 % of the total area) largely coincide with the most eutrophic part of the lake (Tallberg et al. 1999). Lake Tuusulanjärvi is in its entirety less than 10 m deep, and anoxic conditions elsewhere than in the lake deep are rare.

Although the sediment of Lake Vesijärvi mostly has been regarded as an efficient sink for P during aerobic conditions, due to namely the high content of Fe- and Al-oxides (Liukkonen et al. 1993, Hartikainen et al. 1996), the epilimnetic concentration of total P is often characterised by a peak in early June (Kairesalo et al. 1999). Lake Vesijärvi was also the only one of the studied lakes where a clear increase in the hypolimnetic concentration of dissolved P was measured at the time of the sedimentation of the spring bloom (VII). Although the main reason for the epilimnetic total P peak probably is connected to increases in fish-mediated nutrient loading caused by migrating roach (Horppila et al. 1998, Kairesalo et al. 1999, Koski-Vähälä et al. 2000), the influence of Si-P competition at the sediment surface may be a contributing factor. Other short-term impacts, such as increased mineralisation activity of sediment bacteria (Kairesalo et al. 1995) and high pH values caused by intense phytoplankton blooms (cf. Koski-Vähälä et al. 2000), have also been shown or inferred to increase the release of P under certain conditions. Interactions between Si and P at the sediment surface induced by the sedimentation of massive diatom blooms represent another such factor which may be of local and temporal significance. Compared to the external loading of P (0.15 g m^{-2} a^{-1} = 0.41 mg m^{-2} d^{-1}, Fig. 1) the maximal values for the Si-induced P flux (1.4 mg m^{-2} d^{-1}) are indeed quite high; however, the probably limited time-scale of the Si-induced P flux should be remembered.

Compared to Lake Vesijärvi Lake Hiidenvesi, where the calculated Si pulses were smaller and the potential for Si-induced P desorption quite low (VII), is characterised by a quite different food web structure. Although spring diatom blooms occur, the porosity and organic content of the sediment are low, as is the sediment accumulation rate (0.8 mm a^{-1}; Harjula

1972). The system is characterised by strong recycling of nutrients within the water column, possibly due to the high frequency of resuspension in the shallow areas and/or to the high contribution of invertebrate predators to the higher trophic levels (Horppila et al. 2000). The external loading of P is, also, still quite important (0.15 g m^{-2} a^{-1} = 0.41 mg m^{-2} d^{-1}, Fig. 1), although the differences between different parts of the lakes are big (Tallberg et al. 1999). However, the regularly occurring P maxima in the surface water in late summer (VII, Olin and Ruuhijärvi 1999, Tallberg et al. 1999) have yet to be explained. Like in Lake Vesijärvi, fish migrations from the littoral area may be responsible (T. Malinen and M. Vinni, unpublished information), and release of P from the sediment due to high pH induced by massive cyanobacterial blooms is also possible. However, in Lake Hiidenvesi the minimal Si concentrations in the water column do as a matter of fact frequently occur in late summer, just before this P peak (Fig. 11), and the Si-P interactions at the sediment surface should not be ignored as a causative factor.

In Lake Tuusulanjärvi, the sedimentation rate and the sediment surface layer porosity are high, like in Lake Vesijärvi, but the slightly smaller Fe-sorbed P reserves (Fig. 1) and the bigger diatom cells and higher proportion of other phytoplankton (Fig. 10) cause less potential for high Si-induced P fluxes into the water column. However, the effective utilisation of the dissolved Si content of the water column (Fig. 11) increases the potential for Si-induced P fluxes, as does the shallowness of the lake. Since anaerobic conditions at the sediment surface in the lake deep currently occur frequently (e.g. Sommarlund et al. 1998, Olin and Ruuhijärvi 1999), the Si-induced release of P probably constitutes a relatively small part of the entire internal loading in Lake Tuusulanjärvi at the time being. Further, the external loading of P is still an important factor in the nutrient budget of the lake (2.1 mg m^{-2} d^{-1} = 0.75 g m^{-2} a^{-1}, Fig 1).

The Si-P interactions at the sediment surface have further possible consequences. The availability of Si in the water column and especially the Si:P ratio are known to influence both the growth rates and competitiveness of diatoms as a group and in particular the outcome of the species composition within the diatom group (e.g. Kilham 1971, Holm and Armstrong 1981, Hecky and Kilham 1988, Egge and Aksnes 1992, Brzezinski and Nelson 1996, Nelson and Dortch 1996). As eutrophication proceeds the differences between the cycles of Si and P accentuates the importance of Si: cultural eutrophication normally disproportionately increases the loading of the other nutrients (N and P) compared to that of Si (Officer and Ryther 1980, Conley et al. 1993). It has also been proposed that eutrophication speeds up the semi-permanent burial of siliceous diatom shells in the sediment

through increased production, and thus further decreases the amount of available Si in the water column (Schelske and Stoermer 1971, Conley et al. 1993). The sorption of Si could work in the same direction by increasing the Si bound to the sediment. Such sorption and desorption mechanisms do in fact constitute a buffering mechanism by which the relatively low variation in the dissolved Si content of - particularly - rivers and sediment interstitial waters have been explained (e.g. Edwards and Liss 1973, Aston 1983).

However, the concentrations of Si in the interstitial water are, mostly, so high relative to that of the hypolimnion that the Si release from the sediment into the water column is controlled by diffusion rates (e.g. Aston 1983). This study did not uncover any direct evidence in favour of the permanent depletion of the Si content of the water column in the studied lakes, although the scarcity of data on Si do not permit any definite conclusions. In Lake Vesijärvi, there is some evidence in favour of an increase in the annual average biomass of diatoms during the 1990s (Liukkonen et al. 1997, Keto and Tallberg 2000). However, since a biomanipulation project in 1989-1993 removed more than 1000 metric tons of fish and the cyanobacterial blooms all but disappeared (Horppila et al. 1998), a multitude of factors affected the phytoplankton development during this period of time. In Lake Hiidenvesi and Tuusulanjärvi, the data series presented here are obviously too short for any conclusions.

The sorption-desorption mechanisms of Si and P are most likely mainly important as an accentuating factor in the short-term - i.e. within one productive season - cycling of nutrients. More data on the temporal variation of dissolved Si in freshwater lakes could clarify the larger implications of the Si-P interactions studied here, but it is unfortunately seldom routinely available. A further interesting twist to the process is, however, the fact that phytoplankton blooms raise pH, and that both the Si-induced release of P (V) and the competitiveness of cyanobacteria (Paerl and Ustach 1982, Shapiro 1990) are enhanced at high pH. Cyanobacteria are frequently the main nuisance-bloom-forming species of algae which replace the diatoms as eutrophication changes the conditions of the water ecosystem (e.g. Paerl 1988, Sas 1989). In Lake Hiidenvesi, the cyanobacterial blooms in the late summers of 1998 and 1999, which caused very high pH values (unpublished data), were also accompanied by an unexplained increase in the dissolved (and total) P in the water column. The high pH might thus promote the sorption of Si to and release of P from the sediment, and the release of P could refuel the cyanobacterial bloom, keeping pH at a high level. Under such circumstances, the Si-induced release of P could become a more important contributing factor to the internal loading of P.

6. Summary and conclusions

Although the chemistry and biogeochemistry of the element Si have been extensively studied, there are still aspects of the Si cycle which are insufficiently known. This is especially true for the connections between the chemical and biological cycles of Si and the aspects of the Si cycle in water ecosystems where both the water column and the sediment are involved.

Research on the methodology concerned with the short-term mobility of Si in surface sediment is clearly needed. Freezing samples before Si analysis is not advisable, and while the mechanism involved apparently is complexion or polymerisation of Si in a manner resembling dehydration (Tan 1994), with the particulate material in the sample governing the magnitude of the immobilisation of Si, the specific processes involved were only imperfectly clarified in these experiments. Although the high content of native Si also poses problems for quantitative studies on the mobility of Si in sediment, the use of the ^{68}Ge isotope as a marker for Si in sediment posed too many problems to be unconditionally advisable, especially since Si isotopes and the methodology necessary to utilise them in research are getting more readily available (e.g. Brzezinski and Philips 1997). Caution is also required when fractionation procedures designed for P are used to extract Si from sediment, since e.g. dilute NaOH may extract not only adsorbed but also biogenic Si (DeMaster 1981, Conley 1998).

While the interactions between Si and P at soil particle surfaces have been studied (Obihara and Russell 1972, Smyth and Sanchez 1980, Ma and Takahashi 1991), the phenomenon has not hitherto received much attention in limnological research (but see Mortimer 1941, 1942, Brinkman 1993, Hartikainen et al. 1996). These experiments show that Si is capable of influencing the dissolved P content of surface sediment under laboratory conditions. Inorganic Si additions clearly increased the concentration of labile P in surface sediment in a manner characteristic of desorption (cf. House et al. 1998). The process also closely resembled the desorption induced by high pH (e.g. Andersen 1975, Lijklema 1977, Boström et al. 1982), and the increase in labile P could be traced to a decrease in P on hydrated Fe- and Al-oxide surfaces, where the main part of the labile inorganic P in sediment is sorbed by the ligand exchange mechanism (e.g. Hartikainen 1979).

Although it in temperate lakes is unlikely that any other event than the sedimentation of diatom blooms brings sudden large amounts of Si into the surface sediment environment, such events are however very common and often massive (e.g. Smayda 1970, Reynolds

1984). In Lake Vesijärvi, the spring bloom is often dominated by small, comparatively easily dissolved (e.g. Sommer 1984) centric *Stephanodiscus* species (Liukkonen et al. 1993, 1997). The experimentally induced mobilisation of P into the sediment interstitial water caused by settled material rich in such diatom cells strongly indicate that the proposed pathway of Si input to the sediment surface is viable. Field data on the magnitude of the diatom bloom, the utilisation of Si in the water column, and on the disappearance of recognisable diatom frustules from surface sediment further show that the Si release from diatoms at the sediment surface may cause substantial Si pulses within a short period of time.

The internal loading of P from the sediment can be a serious problem in, especially, lakes with large internal P reserves recovering from cultural eutrophication (e.g. Sas 1989). Diatom-derived silicate may induce competitive desorption of P from sediment in eutrophicated lakes, and this phenomenon may under certain conditions be quite a significant source of dissolved P to the water column. The magnitude of the Si-induced release of P depends both on the amount of Fe- and Al-oxides in the sediment and on the P adsorbed to them, and on the Si cycle in the lake: i.e. on the occurrence of large-scale diatom blooms and on the species composition and sedimentation of these. Although the sorption and desorption of Si also might influence the dissolved Si concentration in the water column (Edwards and Liss 1973), there was little direct evidence in favour of the permanent depletion of the Si content of the water column in the studied lakes. The sorption-desorption competitive interactions of Si and P are probably an important factor mainly in the short-term (< 1 year) cycling of nutrients. The potential influence on the phytoplankton species succession (e.g. on the competition between diatoms and non-siliceous phytoplankton) and the interconnection of Si-P sorption mechanisms, pH and phytoplankton blooms are very interesting questions which merit further study.

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